THE THERMAL DECOMPOSITION OF BENZYL IODIDE

John Stobie Gow

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at the
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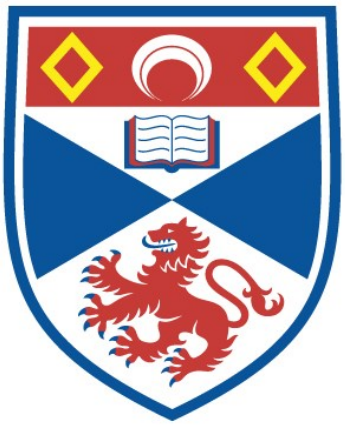

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THE THERMAL DECOMPOSITION OF BENZYL IODIDE

A Thesis presented by

John Stobie Gow, B.Sc.,

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DECLARATION

I hereby declare the following Thesis to be a record of experiments carried out by me, and furthermore, that the Thesis is my own composition and has not been previously presented in application for a Higher Degree.

The investigations were carried out in the Chemical Research Laboratories of the United College, St. Andrews, under the supervision of Dr. Charles Horrex.

UNIVERSITY CAREER

I entered the United College of the University of St. Andrews in October 1951 and graduated as a Bachelor of Science, with First Class Honours in Chemistry, in July 1955.

The research described in this Thesis was carried out in the United College under the direction of Dr. Charles Horrex within the period August 1955 to September 1958.

CERTIFICATE

I hereby certify that Mr. J.S. Gow has spent twelve terms at research work under my direction, that he has fulfilled the conditions of Ordinance No.16 (St. Andrews) and that he is qualified to submit the accompanying Thesis in application for the Degree of Doctor of Philosophy.

Director of Research

ACKNOWLEDGEMENTS

I wish to record my thanks to Dr. Charles Horrex for his assistance, advice and encouragement in all the aspects of this investigation and to Dr. G.W. Downs for many helpful discussions.

I also wish to express my gratitude to Professor John Read, F.R.S., for the provision of research facilities and to the Carnegie Trust for the award of a Scholarship.

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LIST OF ABBREVIATIONS USED IN THE THESIS

Bz	=	The benzyl radical
E_A	=	Activation energy of process (A)
k_A	=	Rate constant of reaction (A)
k cals.	=	1,000 calories
log	=	Logarithm to the base 10
ln	=	Logarithm to the base e
(A)	=	Concentration of component A
pp	=	Partial pressure

INTRODUCTION

AND

REVIEW OF PREVIOUS WORK

INTRODUCTION

A considerable amount of work has been published on the thermal and photochemical decomposition of organic iodides. These substances are, indeed, attractive as subjects for kinetic investigations because the carbon bonds are weak and preferential fission of these links is a possible initiating step in the overall process of decomposition.

Benzyl iodide is a particularly suitable substance for study in this respect since not only is its carbon iodine bond weak but the benzyl radical is an entity of moderate stability. When radicals of marked reactivity are produced, a kinetic analysis can be complicated by the number of possible secondary reactions which can take place. However in spite of its apparently obvious advantages, only one previous study[1] of the gas phase thermal decomposition of benzyl iodide has been made and details were not published in the literature. The work was done by Szwarc who used a flow system with low pressures and short contact times, after the manner of previous studies of iodide pyrolyses by Butler and Polanyi[2]. Szwarc found that the reaction was not first order and suggested, from his data, that the fission process $BzI \longrightarrow Bz\cdot + I$ was followed to some extent by the reverse recombination process. Experimentally, Szwarc was unable to test this by adding iodine to the decomposing benzyl iodide since his reactant injection techniques were not sufficiently controllable.

One of the first objectives of the present work was to establish accurately the kinetic laws under similar conditions by the use of

refined techniques. In the following pages, this work is reported together with studies of several variations of experimental conditions. The general aim of these variations was to obtain data from which a value of the carbon-iodine bond dissociation energy might be obtained. This quantity is of interest as part of the growing knowledge of bond energy values and also because its evaluation permits the heat of formation of the benzyl radical to be deduced. At present, this is a topic about which there is much dispute and independent methods of obtaining it are very important.

Before describing in detail the experimental procedures and results, a survey is given of topics in the literature which are relevant to the discussion of the thermal decomposition of benzyl iodide.

THE DECOMPOSITION OF ORGANIC IODIDES

Since carbon-iodine bonds, in general, are much weaker than carbon-carbon bonds and, as a result, might be expected to favour single bond rupture, the organic iodides have proved interesting subjects for bond strength investigations. The usual products of the decomposition of an iodide of the general formula $R{\cdot}CH_2{\cdot}CH_2{\cdot}I$ are $R{\cdot}CH = CH_2$, $R{\cdot}CH_2{\cdot}CH_3$, $R{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}R$, I_2 and HI. Although it is not possible to determine the mechanism of an iodide's decomposition merely by identifying the end products, the mechanism can often be inferred from a detailed kinetic analysis.

The mechanisms by which iodides decompose and many of the experimental results in the literature have been collated by Steacie[4].

A brief review of some of the reactions involved, with particular reference to the case of benzyl iodide, is given below.

Initiation Reactions

There appear to be two possible primary steps in the decompositions, either the rupture of the carbon-iodine bond to give an organic free radical and a free iodine atom or the disproportionation of the iodide to give an unsaturated hydrocarbon and hydrogen iodide. Many iodides, such as methyl, trifluoromethyl, phenyl, and benzyl cannot decompose to give an olefine while others, such as tertiary butyl iodide, are considered to decompose entirely to the olefine and hydrogen iodide.

(a) The occurrence of reactions of the type $RI \longrightarrow R + I$

Early work by Polanyi et al[2, 3] attempted to produce values for the carbon-iodine bond strengths in a series of organic iodides. Their primary objective was the review of a large number of compounds with the intention of determining trends in the bond strengths in order to correlate them with molecular structures. Polanyi assumed extensively that by using a fast flow system with low partial pressures and low percentage conversions he could obtain kinetic data free from secondary disturbances, and therefore made the assumption that the rate determining step was the split of the carbon-iodine bond and that the energies of activation obtained were equivalent to the bond energies. If his

assumptions are correct then the energies of activation so obtained do give the relation of bond dissociation energy to molecular structure. On the whole, the answers he obtained seem reasonable, e.g. a variation from 54 K cal for methyl iodide to 44 K cal for benzyl iodide. However, later data, also obtained by fast flow techniques, show that, in many cases, the decomposition kinetics are much more complicated than Polanyi assumed. Szwarc[1], investigating the pyrolysis of benzyl iodide, showed that true first order kinetics were not obtained. The occurrence of a strong reverse reaction was postulated by Szwarc, who put forward the mechanism

$$BzI \longrightarrow Bz\cdot + I \qquad (1)$$

$$M + I + I \longrightarrow I_2 + M \qquad (2)$$

$$2\ Bz\cdot \longrightarrow Bz - Bz \qquad (3)$$

to account for his results. Calculations on this basis lead to a tentative value of 39 K cal/mol. for the energy of activation of the decomposition reaction. No experimental evidence of the postulated reverse reaction was presented by Szwarc. Horrex and Lapage[5] and Cundall and Horrex[6] have used the fast flow technique extensively to study the decomposition of methyl iodide. Experiments

were carried out at both high and low pressures, with toluene being used to eliminate the reverse reaction. Both Lapage and Cundall presented evidence for first to second order transitions, the decomposition being apparently first order in the region of 600 mm. pressure. They showed that, under first order conditions, the rate constant for the decomposition was given by $k = 2.6 \times 10^{13} \times e^{-\frac{54,700}{RT}}$. Using both toluene and hydrogen iodide as radical acceptors, Downs and Horrex[7], in a study of the decomposition of trifluoromethyl iodide, found that the initial split into a trifluoromethyl radical and an iodine atom had an energy of activation of 53.5 K cal/mol.

In addition to the flow technique data, quoted above, a substantial amount of work has been done using static systems. These involve the type of conditions which Polanyi et al[2] attempted to avoid, i.e. opportunities for reactions of the type $R\cdot + I_2 \longrightarrow RI + I$ etc. as the iodine concentration increases. In particular, Ogg has investigated the decomposition of many iodides, both alone and in the presence of HI in static systems. Amongst those investigated by Ogg, methyl[8], ethylene[9], n-propyl[10],

iso-propyl[11] and sec-butyl[12] iodides were all assumed to include a simple rupture of the carbon-iodine bond as a contributing reaction. In general, Ogg concluded that the carbon iodine bond strength varied little from one compound to another and usually had a value of about 43 K cal/mol. This conclusion seems exceedingly unlikely in view of the known differences in reactivity of the various iodides and therefore some doubt must be cast on Ogg's mechanisms. As an example of the type of mechanism, proposed by Ogg, that for methyl iodide[8], in the presence of hydrogen iodide, may be considered. For this system, he proposed

$$CH_3I \longrightarrow CH_3 + I \qquad (4)$$

$$HI + CH_3I \longrightarrow CH_4 + I \qquad (5)$$

$$CH_3 + HI \longrightarrow CH_4 + I \qquad (6)$$

$$CH_3 + I_2 \longrightarrow CH_3I + I \qquad (7)$$

$$2\ I + M \longrightarrow I_2 + M \qquad (2)$$

Ogg deduced that (4) was first order at pressures in excess of 50 mm. and quoted k as $3.9 \times 10^{12} \times e^{-\frac{43,000}{RT}}$ sec.$^{-1}$ Because of the results obtained in the present investigation and also those of Downs and Horrex[7] on the decomposition of trifluoromethyl iodide, in neither of which any

bimolecular reaction similar to (5) was observed, it seems unlikely that the observed dependence of the rate on the hydrogen iodide concentration is attributable to such a step. A probable explanation is that in the absence of a large excess of hydrogen iodide, reaction (6) does not entirely preclude the reverse reaction (7). Almost precisely this interpretation has recently been put on Ogg's results by Benson and O'Neal[13].

(b) <u>The occurrence of reactions of the type</u>
<u>$R{\cdot}CH_2{\cdot}CH_2{\cdot}I \longrightarrow R{\cdot}CH = CH_2{\cdot} + I$</u>

The most clearly established example of this type of reaction is the decomposition of t-butyl iodide into iso-butylene and hydrogen iodide. In a case, such as this, the only likely subsequent reaction is the addition of hydrogen iodide to the olefine to reform the parent iodide. According to Jones and Ogg[14], this reverse reaction does take place with t-butyl iodide and an equilibrium is set up.

<u>Subsequent Reactions</u>

When the primary step is a split into a radical R and an iodine atom there are several possible subsequent reactions. These may be summarised as follows:-

(a) an iodine atom may react with the parent molecule to give a free radical and an iodine molecule

(b) the radicals may dimerise or disproportionate into an olefine and a paraffin

(c) the radical may react with iodine atoms of molecules to reform the parent iodide

(d) the radical may attack the parent iodide according to either $R + RI \longrightarrow R\text{-}R + I$ or $R + RI \longrightarrow R\text{-}H + R^1$ where R^1 contains an iodine atom and may take part in subsequent reactions

(e) an iodine atom may react with a free radical to give an olefine and hydrogen iodide

(f) the organic radical can decompose into an olefine and a hydrogen atom which may subsequently attack the parent iodide

(g) iodine atoms will take part in the normal equilibrium $I + I \longleftrightarrow I_2$

Only a limited number of these reaction types is likely in the case of benzyl iodide since disproportionation reactions of the benzyl radical are unknown. There is, however, a great deal of evidence for the occurrence of reactions of the types (a), (b), (c) and (g) which are all likely to occur during the decomposition

of benzyl iodide. A review of some of this evidence will be given here.

(i) Occurrence of reactions of the type $I + RI \longrightarrow R + I_2$

The decomposition of several iodides has been found to be at least partially an iodine catalysed reaction, the rate being given by an expression such as

$$-\frac{d(RI)}{dt} = k(RI)(I_2)^{\frac{1}{2}}$$

N-propyl[10] and iso-butyl[11] iodides were found by Ogg to obey such an expression. Ogg put forward the following reaction sequence to account for this result.

$$C_3H_7I \longrightarrow C_3H_7 + I$$
$$C_3H_7 + C_3H_7I \longrightarrow C_3H_8 + C_3H_6I$$
$$C_3H_6I \longrightarrow C_3H_6 + I$$
$$n\text{-}C_3H_7I \longrightarrow n\text{-}C_3H_7 + \tfrac{1}{2} I_2$$
$$n\text{-}C_3H_7 + I_2 \longrightarrow iso\text{-}C_3H_7 + I$$
$$iso\text{-}C_3H_7I \longrightarrow \tfrac{1}{2} C_3H_8 + \tfrac{1}{2} C_3H_6 + \tfrac{1}{2} I_2$$
$$2\,I + M \longrightarrow I_2 + M$$

However, Schumacher[15] has criticised Ogg's mechanism and suggested that the reaction $n\text{-}C_3H_7I + I \longrightarrow iso\text{-}C_3H_7 + I_2$ was the cause of the observed iodine dependence. Schumacher proposed the sequence

$$C_2H_4I_2 \longrightarrow C_2H_4I + I \qquad (8)$$

$$I_2 \longrightarrow I + I \qquad (9)$$

$$C_2H_4I_2 + I \longrightarrow C_2H_4I + I_2 \qquad (10)$$

$$C_2H_4I \longrightarrow C_2H_4 + I \qquad (11)$$

$$C_2H_4I + I_2 \longrightarrow C_2H_4I_2 + I \qquad (12)$$

Provided that $\frac{k12}{k11(I_2)}$ is small compared with unity, this sequence gives Arnold and Kistiakowsky's experimental rate equation.

This type of iodine atom reaction with the parent molecule has also been found in the thermal and photochemical iodine exchange reaction of the allyl and benzyl iodides. Noyes and his collaborators in a series of papers reported the exchange of radioactive iodine with ethylene[17, 18, 19], sec-butyl[20], allyl[21, 22] and benzyl iodides[23]. In the case of benzyl iodide, the reaction between the iodide and radioactive iodine was studied in solution in hexachlorobut-1:3-diene at temperatures between 60 and 90°C. The exchange of the isotopically labelled iodine was found to obey an expression of the form $R = k(BzI)\ (I_2)^{\frac{1}{2}}$. Gazith and Noyes[23] suggested that the mechanism was:-

$$BzI \longrightarrow Bz + I \qquad (S1)$$

$$I_2 \longrightarrow I + I \qquad (S2)$$

$$I + BzI \longrightarrow Bz + I_2 \qquad (S3)$$

$$Bz + I_2 \longrightarrow BzI + I \qquad (S4)$$

$$I + I \longrightarrow I_2 \qquad (S5)$$

$$Bz + I \longrightarrow BzI \qquad (S6)$$

$$Bz + Bz \longrightarrow Bz\text{-}Bz \qquad (S7)$$

and evaluated all seven of the rate constants at 36°C. They deduced that the carbon-iodine bond in benzyl iodide is 1.9 K cal/mol. stronger than the bond in molecular iodine i.e. 37.4 K cal/mol. The value of k_3 was quoted as 7.1×10^4 l. mol.$^{-1}$ sec.$^{-1}$ and k_4 as 3.3×10^6 l. mol.$^{-1}$ sec.$^{-1}$. If it is assumed that the energy of activation of reaction (S3) is equal to its endothermicity i.e. 1.9 K cal/mol. (this is equivalent to assuming that the energy of activation of reaction (S4) is zero), then the pre-exponential factor may be calculated. Such a calculation leads to the conclusion that the attack of an iodine atom on a benzyl iodide molecule has a P (or steric) factor of the order of 10^{-4} to 10^{-5}.

(ii) Occurrence of reactions of the type $R + R \longrightarrow R\text{-}R$

Although a great deal of evidence exists for the occurrence of the simple dimerisation of organic free radicals, these reactions are difficult to study directly. The main difficulty in evaluating the rate of such a reaction is the lack

of knowledge of the concentration of the radicals. For the case of the dimerisation of methyl radicals, two methods have been employed to circumvent this difficulty. Marcus and Steacie[24] and Miller and Steacie[25] have carried out experiments in which the reaction between methyl radicals and nitric oxide competes with the dimerisation reaction. Since the rate of the reaction $CH_3 + NO \longrightarrow$ products had been assessed in separate experiments by Forsyth[26] and later by Durham and Steacie[27], the rate of recombination of methyl radicals could be calculated. Gomer[28] and Gomer and Kistiakowsky[29] investigated the life time of methyl radicals in a static system by the intermittent irradiation of mercury dimethyl. Both approaches showed that the energy of activation of recombination was approximately zero and Steacie[4] concluded that both sets of experiments were compatible with a collision efficiency of about 0.3.

Similar dimerisation reactions of trifluoromethyl[30], ethyl[31], n-butyl[32] and phenyl[33, 34] radicals have been described and in all of these very low or zero energies of activation have been assumed. The combination

of two benzyl radicals to form dibenzyl has frequently been shown to occur e.g. in the thermal decomposition of tin dibenzyl[35] and mercury dibenzyl[36] the product is dibenzyl. Furthermore, in many of the reactions investigated by the toluene carrier technique, dibenzyl is formed, indicating that the recombination of two benzyl radicals occurs readily. In their examination of the iodine exchange reaction with benzyl iodide, Gazith and Noyes[23] calculated the rate of combination of benzyl radicals as 1.6×10^9 l. mol^{-1} sec.

(iii) Occurrence of reactions of the types
$R + I_2 \longrightarrow RI + I$ and $R + I \longrightarrow RI$

The most comprehensive evidence for the occurrence of reactions of this type has been provided by studies of the photolytic decomposition of iodides. Investigations of the photolysis of methyl iodide by West and Ginsberg[37], West and Schlessinger[38] and Bates and Spence[39, 40] all showed that very low quantum yields were obtained, presumably due to the efficiency of a recombination reaction. West and Schlessinger considered that the reverse reaction was $CH_3 + I \longrightarrow CH_3I$ but Bates and Spence

reported that $CH_3 + I_2 \longrightarrow CH_3I + I$ was also important. Williams and Ogg[41] photolysed methyl iodide in the presence of hydrogen iodide and tacitly assumed that the reverse reaction involved a methyl radical and iodine molecule. Iredale[42], whose evidence for the existence of a strong reverse reaction was based on the increase in the quantum efficiency when nitric oxide was added to the system, considered both forms of the reverse reaction to be important. (Iredale and McCartney[43] demonstrated that the quantum efficiency did reach unity when sufficient nitric oxide was added). In an attempt to distinguish between the two types of reaction, Anderson and Kistiakowsky[44] photolysed methyl iodide in the presence of added iodine and hydrogen bromide. In this system the possible methyl radical removing reactions were

$$CH_3 + I \longrightarrow CH_3I \qquad (13)$$

$$CH_3 + I_2 \longrightarrow CH_3I + I \qquad (7)$$

$$CH_3 + HBr \longrightarrow CH_4 + Br \qquad (14)$$

and the disappearance of the radical would be given by $R = k_{14}(HBr)(CH_3) + k_{13}(CH_3)(I) + k_7(CH_3)(I_2)$. From their experimental results, Anderson and Kistiakowsky concluded that the reaction of the radical with an iodine atom was unimportant. This

conclusion would not necessarily be valid in experiments with methyl iodide alone in which no excess of molecular iodine would exist. In a similar way to the work on methyl iodide, Dacey[30] has studied the photochemical decomposition of trifluoromethyl iodide. Once again low quantum efficiencies, which could be increased by the presence of silver of nitric oxide, were obtained. Dacey attributed the low yields to the occurrence of both forms of the reverse reaction.

In a summary of all the published work on the decomposition of organic iodides, Steacie[4] has stated that the mechanism can usually be represented by:-

$$RI \longrightarrow R + I$$

$$R + RI \longrightarrow RH + R^1 \qquad (15)$$

$$R^1 \longrightarrow \text{Olefine} + H$$

$$I + I \longrightarrow I_2$$

$$R + I \longrightarrow RI$$

with $R + I_2 \longrightarrow RI + I$ occurring at higher percentage decompositions. In the case of benzyl iodide, however, no reaction akin to reaction (15) occurs since neither toluene nor stilbene has been observed in the products of its decomposition. The steric hindrance involved in such a reaction and the relative stability of the benzyl radical

may well be the reasons for the failure of this type of reaction to occur. The high efficiency of the reverse reaction may also be a contributing factor.

PREVIOUS DETERMINATIONS OF BENZYL-X BOND STRENGTHS

The bond dissociation energy of all benzyl compounds can be related to the heat of formation of a benzyl radical if the relevant thermochemical data are known. The equation relating the two quantities is

$$D(Ph\cdot CH_2\text{-}X) = -\Delta Hf(Ph\cdot CH_2\text{-}X) + \Delta Hf(Ph\cdot CH_2\text{-}) + \Delta Hf(X)$$

In the case of toluene, for example, the heat of formation of toluene and of a free gaseous hydrogen atom are well established and thus, if the bond dissociation energy is measured, the value of the heat of formation of the benzyl radical can be deduced.

A review of the data available to them on the bond strength of benzyl-X compounds has recently been given by Benson and Buss[47]. They tabulate values of the heat of formation of the benzyl radical as derived from the various bond strengths and the appropriate thermodynamic data. A selection of this data is presented in Table 1.

The range of values obtained for the heat of formation of the radical casts considerable doubt on the values of certain of the bond strengths quoted and probably on some of the thermodynamic data used. Therefore a few comments on the methods of determination of some of the more important benzyl compound bond

Table 1

Reaction	E_T K cal	ΔH_{298} K cal	ΔH_f° (Bz)
$Ph{\cdot}CH_2H \longrightarrow Bz + H$	77.5	77.8	37.8
$Ph{\cdot}CH_2{\cdot}Br \rightarrow Bz + Br$	50.0	51.3	43
$Ph{\cdot}CH_2{\cdot}NH_2 \rightarrow Bz + NH_2{\cdot}$	59	60.5	30.1
$Ph{\cdot}CH_2{\cdot}CH_3 \rightarrow Bz + CH_3{\cdot}$	63.2	64.5	39.6
$Ph{\cdot}CH_2{\cdot}C_2H_5 \longrightarrow Bz + C_2H_5{\cdot}$	57.5	58.8	33.8
$Ph{\cdot}CH_3 \longrightarrow Bz^+ + H + e^{-1}$		95	55

strengths seem appropriate.

Toluene

The commonly quoted value for the bond strength of toluene of 77.5 K cal was obtained by Szwarc[48] using a fast flow technique. He claimed that the decomposition was first order and could be represented by

$$k \text{ sec.}^{-1} = 2 \times 10^{13} \exp - \frac{77,500}{RT}$$

The value of 77.5 K cal/mol. was assigned by Szwarc to the carbon-hydrogen bond strength. However, Blades, Blades and Steacie[49] have criticised Szwarc's postulated mechanisms and have shown the decompositions to be much more complex than he assumed. Although Steacie et al. did not exactly repeat Szwarc's work, in that they used a higher temperature and much shorter contact times, it seems unlikely that Szwarc's mechanism is correct and therefore his

value of the bond energy must be in doubt. Steacie was not prepared to deduce a value for the bond energy from his data but pointed out that a plot of an assumed first order rate constant against $\frac{1}{T}$ gave an energy of activation in the region of 90 K cal/mol.

A totally different and unfortunately much less direct method was employed by Anderson, Sheraga and Van Artsdalen[50] who studied the thermal and photochemical bromination of toluene. Their derived value for the toluene bond strength is 89 K cal. which is probably best regarded as an upper limit. As Van Artsdalen points out, the difference between his value and Szwarc's is such that further investigations, by independent means, are required. It may be noted that, using well established thermochemical data, the heat of formation of the benzyl radical may be calculated as 37.5 K cal using Szwarc's value and 49.5 K cal using that of Van Artsdalen.

Attempts have been made to use the electron impact method to decide between the two extreme values of the toluene bond strength. An apparent confirmation of Szwarc's value was obtained by Schissler and Stevenson[51] who measured the appearance potential of the $C_7H_7^+$ ions from both toluene and dibenzyl. Using these two appearance potentials in conjunction with known thermochemical data, they calculated $D(Ph{\cdot}CH_2{-}H)$ as 77 ± 3 K cal/mole. This appears to be excellent confirmation of the work of Szwarc but, unfortunately, the values of the appearance potentials obtained by

Schissler and Stevenson have been questioned by Farmer et al.[52]. Farmer, using Schissler and Stevenson's values for the appearance potentials and the appropriate heats of formation, calculates the ionisation potential of the benzyl radical as 8.51 e.v. A direct measurement of this ionisation potential by Lossing, Ingold and Henderson[53] gives the value as 7.8 e.v. Further evidence of complicating factors is presented by Farmer et al. in their experiments on the ionisation of trideuterotoluene. The ions $C_7H_5D_2^+$ and $C_7H_4D_3^+$ were produced in the statistical amounts demanded by the assumption that all the hydrogen atoms are equivalent in the dissociation process. Similar conclusions have been reached by Rylander, Meyerson and Grubb[54], who examined the mass spectra of $Ph{\cdot}CH_3$, $Ph{\cdot}CH_2D$ and $Ph{\cdot}CD_3$, except that the latter conclude that the $C_7H_7^+$ ion is neither the benzyl nor the tolyl ion, as suggested by Farmer, but in fact the tropylium ion. It is evident that whatever the true nature of the dissociation process may be, it is not the simple process it has been assumed to be and therefore the agreement between Schissler and Stevenson's value for the carbon-hydrogen bond strength and that of Szwarc must be regarded as fortuitous.

A recent application of the equilibrium method to the bromination of toluene has been made by Benson and Buss[47]. They measured the equilibrium constant for the reaction

$$Ph{\cdot}CH_3 + Br_2 \longrightarrow Ph{\cdot}CH_2\text{-}Br + H\text{-}Br$$

at 425°K and used their value of the equilibrium constant to

calculate the associated change of free energy. Using a calculated value of the entropy of benzyl bromide, they obtained the change in heat content of the reaction by use of the equation $\Delta G^{\circ} = \Delta H^{\circ} - T\,\Delta S^{\circ}$. This ΔH° is related to the bond strength of toluene by the equation

$D(Ph{\cdot}CH_2\text{-}H) - D(Ph{\cdot}CH_2\text{-}Br) = \Delta H^{\circ} + D(H\text{-}Br) - D(Br_2)$.

Although the values of D(H-Br) and $D(Br_2)$ in the literature may be considered to be accurate, it is doubtful if the same is true of the value for $D(Ph{\cdot}CH_2\text{-}Br)$. Benson and Buss used the value of Szwarc, Gosh and Sehon[55] of 50.5 K cal and hence evaluated $D(Ph{\cdot}CH_2\text{-}H)$ as 84 K cal/mole - this leads to a value of 44.9 K cal for the heat of formation of the benzyl radical.

Dibenzyl

If an accurate value for the central carbon-carbon bond in dibenzyl can be obtained then this is obviously an ideal bond strength from which to calculate the heat of formation of a benzyl radical. Since two such radicals are formed from each molecule of dibenzyl the accuracy of the deduced radical heat of formation will be doubled.

Horrex and Miles[56] investigated the pyrolysis of dibenzyl in a flow system at temperatures between 630°C and 774°C. They found that the overall reaction could be represented by

$3\ Ph{\cdot}CH_2\text{-}CH_2{\cdot}Ph \longrightarrow 2Ph{\cdot}CH_3 + Ph{\cdot}H + Ph{\cdot}CH = CH_2 + Ph{\cdot}CH = CH{\cdot}Ph.$

The overall energy of activation of 48 K cal/mole was associated by them with the strength of the central carbon-carbon bond since they

considered that the rate determining step was the initial split into two benzyl radicals. A re-investigation of this system by Pittilo[57] showed that a recombination of the benzyl radicals took place and that the rate was determined by the rate of attack of a benzyl radical on a parent dibenzyl molecule to form toluene, as well as by the initial split. It was, therefore, considered impossible to assign a bond strength on these studies. However, Alexander[58] recently investigated the pyrolysis of dibenzyl in the presence of hydrogen iodide and found that free iodine was produced at a rate which was first order in dibenzyl and zero order in hydrogen iodide. This he ascribed to the fact that the hydrogen iodide was acting as a radical catcher in a similar manner to the toluene in Szwarc's carrier technique. Unfortunately, Alexander's results were complicated by the occurrence of the reaction $Ph{\cdot}CH_2{-}CH_2{\cdot}Ph + I_2 \longrightarrow Ph{\cdot}CH = CH{\cdot}Ph + 2HI$. Nevertheless, by studying this secondary reaction also, Alexander was able to calculate its effect on the overall reaction and to allow for it in estimating the bond strength of dibenzyl as 61 K cal/mol. Using -29.7 K cal/mol as the heat of formation of dibenzyl, this leads to a value of 45.3 K cal for the heat of formation of the benzyl radical.

A completely different approach to the problem by Davidson[59] leads to a value of 60 K cal/mol. for the central carbon-carbon bond, in excellent agreement with Alexander. Davidson, by means of a high resolution mass spectrometer, followed the dissociation of a mixture of $Ph{\cdot}CH_2{-}CH_2{\cdot}Ph$ and $Ph{\cdot}CD_2{-}CD_2{\cdot}Ph$ under conditions where

the recombination of the radicals and not the decomposition of dibenzyl was the predominant reaction. The actual phenomenon observed was the rate of growth of the peak at mass 184, corresponding to the molecule $Ph{\cdot}CH_2{-}CH_2{\cdot}Ph$. This work gives a value of 44.9 K cal/mol. for the heat of formation of the benzyl radical and this is in such close agreement with the work of Alexander and with that of Benson and Buss[47] that considerable reliance may be placed on this value.

Benzyl Bromide

Szwarc and his co-workers[55] have investigated the thermal decomposition of benzyl bromide using the toluene carrier technique[60] and have assigned the overall energy of activation of 50.5 K cal/mol. to the carbon-bromine bond strength.

An indirect calculation of the bond strength by Gellner and Skinner[61] estimated it as 48.5 K cal/mol., apparently an excellent confirmation of Szwarc's value. However, Gellner and Skinner only obtained a value for the bond strength by assuming a value for the heat of formation of the benzyl radical of 37.5 K cal and this does not therefore constitute an independent check. Indeed, if the data of Davidson[59] and Alexander[58], quoted above, are correct then Gellner and Skinner's data would give a value of 54.1 ± 3 K cal/mol. for the carbon-bromine bond strength. (If the value of ΔH_f (benzyl bromide) is 15.6 as suggested by Gellner and Skinner). Electron impact data by Lossing, Ingold and Henderson[53] give $D(Ph{\cdot}CH_2{-}Br)$ as 44.7 ± 3 K cal. This value seems much too low and

it is probable that the doubts expressed previously as to the validity of the assumption that the $C_7H_7^+$ ion is in fact the benzyl ion account for this low result.

Benzyl Iodide

As will have been realised from the foregoing comments on the bond strength determinations on toluene, dibenzyl and benzyl bromide, there is a great deal of conflicting evidence about the value of the benzyl radical heat of formation.

In the section concerned with the decomposition of organic iodides it was mentioned that Szwarc[1, 62] quotes a value of 39 K cal for $D(Ph\cdot CH_2-I)$ while Gazith and Noyes[23] quote 37.4 K cal/mol. In order to calculate the heat of formation of the benzyl radical from these values it is necessary to have a value for ΔH_f (benzyl iodide). In a recent review on thermochemistry, Skinner[63] suggests that the 'best' value for ΔH_f (benzyl iodide) is 27.2 ± 3 K cal. Using this, the two suggested bond strengths of benzyl iodide are equivalent to 42 K cal and 39.1 K cal respectively.

Once again, electron impact studies have been made in attempts to obtain confirmatory evidence. Lossing, Ingold and Henderson[64] have measured the appearance potential of the $C_7H_7^+$ ion from benzyl iodide and found it to be 9.23 ± 0.05 e.v. Taken in conjunction with the ionisation potential of the ion of 7.73 ± 0.08 e.v.[53], this leads to a value of 34.6 ± 3 K cal for $D(Ph\cdot CH_2-I)$. Unfortunately, the evidence of Rylander et al.[54], already quoted, makes it unlikely

that any reliance can safely be placed on electron impact studies where the benzyl ion is expected to exist.

It is hoped, in the present investigation, to determine the value of the carbon-iodine bond strength by a method similar to that used by Szwarc, except that additional measures will be taken to establish fully the mechanism by which the iodide decomposes.

THE DEFINITION OF BOND DISSOCIATION ENERGY

The bond dissociation energy, D(R-R) of a bond R-R is strictly defined as the change in energy, at absolute zero in the ideal gas state, associated with the reaction $R\text{-}R \longrightarrow R^{\bullet} + R^{\bullet}$, the products being in their ground states. Fortunately the change in enthalpy, measured at normal temperatures, does not differ markedly from the true value of the bond energy. In the case of the dissociation of benzyl iodide into a free radical and an iodine atom, the difference is equivalent to approximately 3/2 RT or about 2 K cal/mol. for determinations at between 300 and 400°C. Only in a very few cases are experimental data sufficiently accurate to justify the application of this correction and even then the necessary heat capacities, required to evaluate the correction accurately, are not always available.

METHODS OF DETERMINING BOND ENERGIES

The successful determination of bond dissociation energies requires an experiment in which energy is supplied to the bond in question under carefully controlled conditions. The necessary energy may be supplied thermally, photolytically, or by a high energy electron

beam. An excellent summary of the available experimental methods has recently been given by Cottrell[45] and it would be superfluous to give here a detailed account of these methods. Therefore, only the kinetic method, which was used in the present investigation will be discussed.

In the kinetic method, the activation energy for the process $R\text{-}R \longrightarrow R^{\bullet} + R^{\bullet}$ is calculated from measurements of the rate of the reaction over a range of temperatures. It is assumed that the reverse reaction involving the recombination of two free radicals has zero energy of activation. Because it is difficult (although possible by means of mass spectrometry) to measure the concentration of free radicals directly, the energy of activation of the initial split has usually to be calculated from a study of the overall reaction. If such a calculation is to be valid then the following conditions must be satisfied:-

(a) the rate determining step should be the breaking of the bond being examined

(b) the mechanism should be conclusively established

(c) all side reactions should be eliminated or their extent accurately assessed.

In the present work, both static and flow techniques have been used to study the thermal decomposition of benzyl iodide. The fast flow technique was used to a greater extent because the very short reaction times involved were expected to eliminate complicating secondary

processes. This method does, however, have some serious disadvantages, e.g.

(1) only a narrow range of reaction times can generally be covered and thus it is not a very suitable method for determining the order of a reaction

(2) the true value of the reaction time is not known with high accuracy. This is a result of the fact that the gas does not attain the temperature of the reactor immediately it enters it nor is the reaction quenched immediately when the reactants leave the tube

(3) no account is normally taken of the effects of diffusion with the gas stream. The assumption that this effect is negligible is probably justified if not more than 5-10% of the reactants are used up as they pass through the tube. In principle, the effect of diffusion can be calculated, using equations due to Forster and Geib[46], although these are difficult to apply in practice.

Although much less use was made of a static system, this method proved extremely valuable for extending the range of temperatures over which the reaction could be studied. Of course much higher concentrations of reactants were necessary with this system than

with the flow system and the possibility of secondary reactions occurring was correspondingly greater. One advantage of the static system is that, with the longer reaction times involved, errors in the measurement of this time are usually negligible.

APPARATUS AND EXPERIMENTAL TECHNIQUE

APPARATUS AND EXPERIMENTAL TECHNIQUE

This section is concerned only with the nature of the apparatus and the techniques employed; the detailed results of the many experiments performed are given in the next section.

Two distinct experimental methods were employed in the present investigation. The main part of the work was done with a flow technique, using total pressures of 10 mm. or less, short reaction times and relatively high temperatures. In order to study the reaction over a wider range of temperature and at higher pressures, a static method was also used for part of the work.

The apparatus used in each method and also the analytical techniques employed will be described, in detail, in the following pages.

(a) FLOW METHOD

The apparatus used was in essence similar to that employed by Butler and Polanyi[2] in their initial investigations on the pyrolysis of organic halides. The method has undergone many modifications and improvements since then and greater experimental accuracy has thereby been attained.

Basically, the method consists of injecting small quantities of the compound under investigation into a stream of inert gas, in this case nitrogen, which is being circulated through a hot tube and then freezing out the products of the decomposition by passing the gas stream through a trap surrounded by either an acetone/solid carbon dioxide mixture or liquid oxygen.

EVACUATION SYSTEM

The entire system could be evacuated, normally to a pressure of 10^{-5}mm. of mercury, by means of a mercury diffusion pump backed by a two stage rotary oil pump. The pressure in the system could be measured by a single high vacuum McLeod gauge.

CIRCULATION SYSTEM

The nitrogen carrier gas was circulated round the apparatus by a triple jet mercury vapour pump. The pump was heated by a Wood's metal bath, the temperature of which was controlled to within $\pm$ 1°C by means of a Sunvic Energy Regulator. The stem of the pump was also heated by winding it with nichrome tape since it has been shown

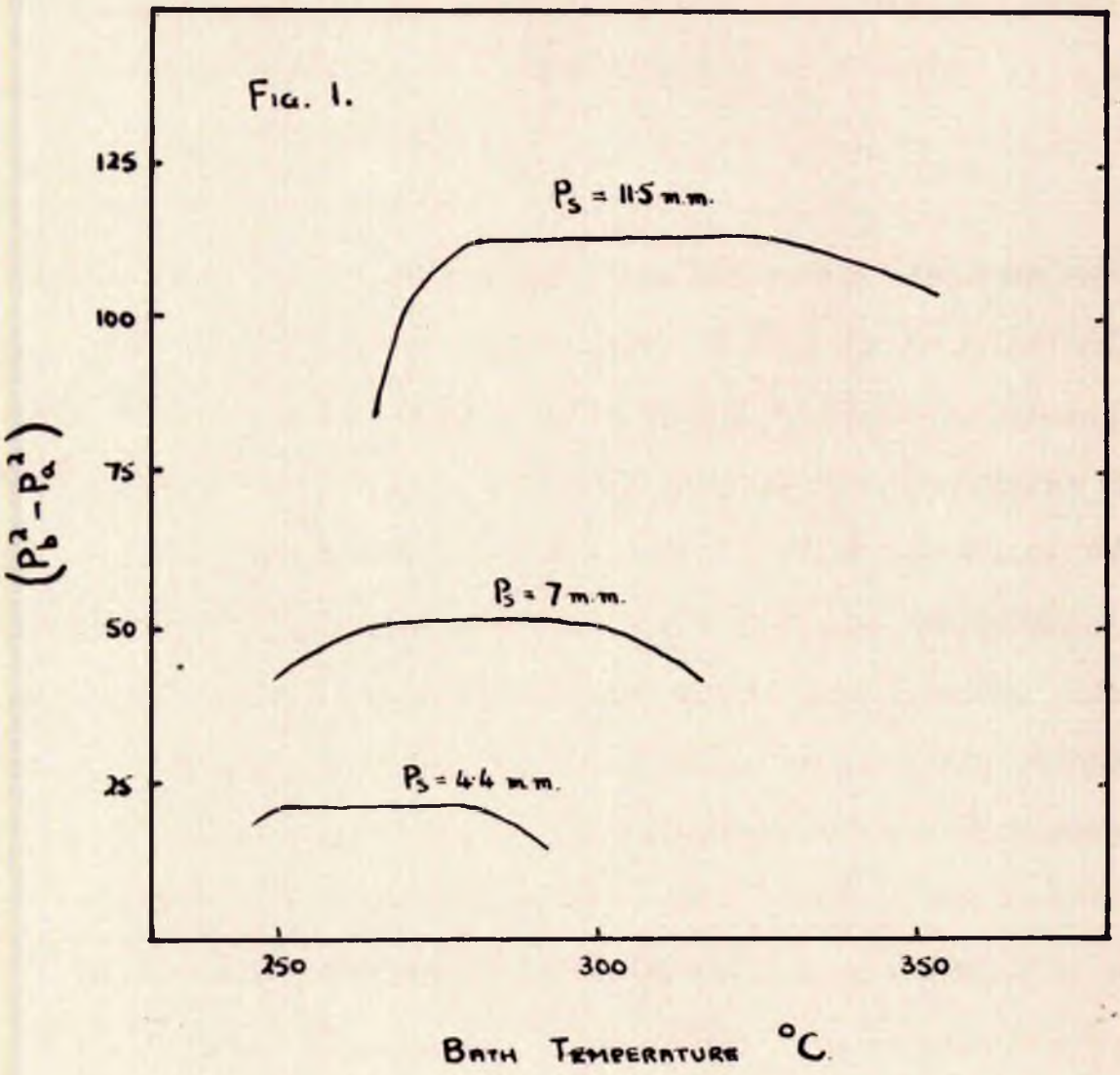


Fig. 1. $(P_b^2 - P_a^2)$ v. Bath Temperature at Various Static Pressures (P_s) of Nitrogen.

by Alexander[58] that this leads to a more constant rate of flow.

It is essential, in this type of system, to select the temperature of the Wood's metal bath so that the rate of flow is not critically dependent on this temperature. There was a considerable range of temperature over which, for a given total pressure of nitrogen, the rate of flow was not significantly altered. In Figure 1, $(P_b^2 - P_a^2)$, which was the difference between the squares of the pressures before and after the capillary, and was directly proportional to the rate of flow, is plotted against the bath temperature. The bath temperature required to produce the optimum pump performance was markedly dependent upon the static pressure of nitrogen and the figure illustrates this dependence.

Variations in the rate of flow at a fixed nitrogen pressure were readily achieved by altering the capillary, two capillaries being fitted in parallel, or alternatively by partially opening a tap which was connected between the inlet and outlet of the circulation pump. By this latter method, it was easy to make small adjustments to the rate of flow and so produce any desired reaction time. It is especially desirable in experiments where the partial pressures of several compounds must be kept constant, that the rate of flow of carrier gas be readily adjustable and the above method proved entirely satisfactory for this purpose.

MEASUREMENT OF RATE OF FLOW AND THE PRESSURE IN REACTION VESSEL

The rate of flow of nitrogen was determined by measuring, on a pair of McLeod gauges, the pressure at each end of a capillary, the dimensions of which were known. Theoretically, by using Meyer's modification of Poiseuille's formula, the rate of flow can then be calculated directly from

$$n = \frac{\pi r^4 (P_b^2 - P_a^2)}{16 \eta LRT}$$

where

- n = moles/sec.
- r = radius of capillary in cms
- P_b and P_a = pressures before and after the capillary expressed in dynes/cm.^{2}
- η = the viscosity of the gas
- L = length of capillary in cm.
- R = the gas constant
- T = absolute temperature

We may therefore write that $n = K (P_b^2 - P_a^2)$ where K is the capillary constant. Table 2 gives the dimensions of the two capillaries and the calculated capillary constants for air, using Partington's[65] values for the viscosity of air.

Table 2

Capillary	Length	Radius	K air x 10^6
Long	13.7 cm.	.1557 cm.	3.410
Short	6.15 cm.	.1557 cm.	7.598

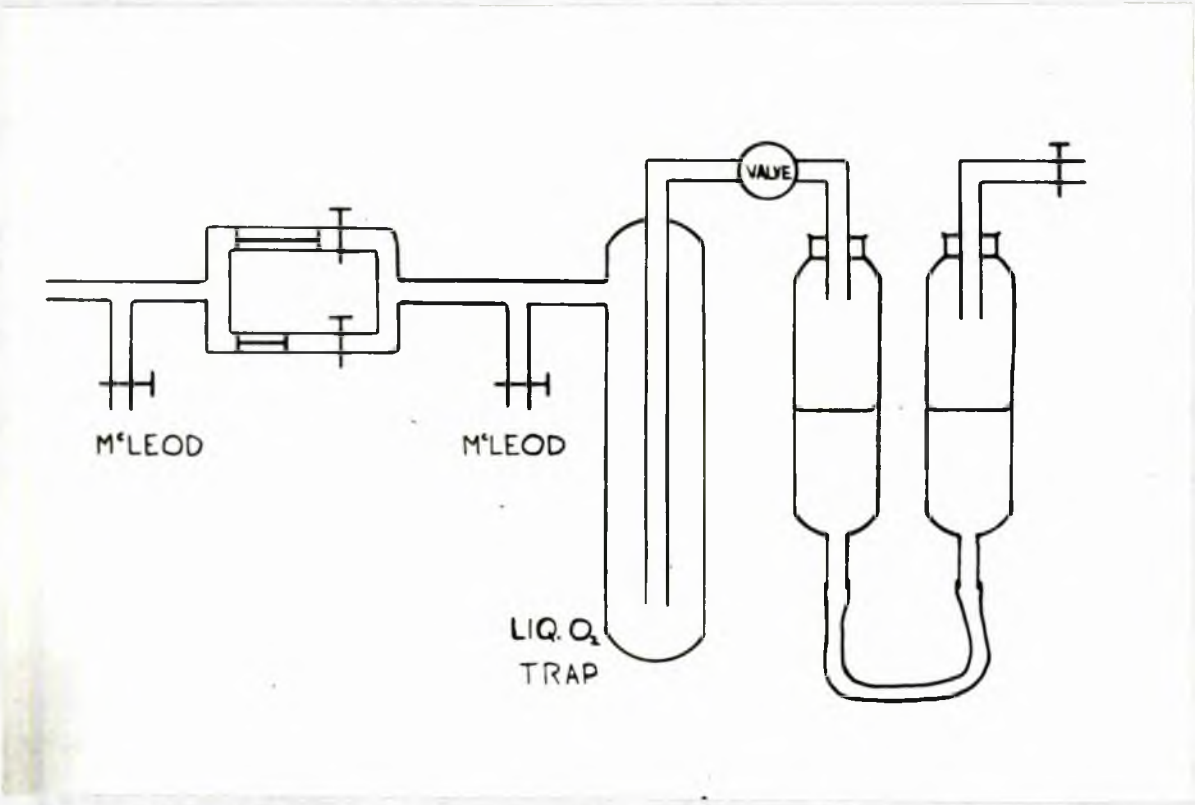
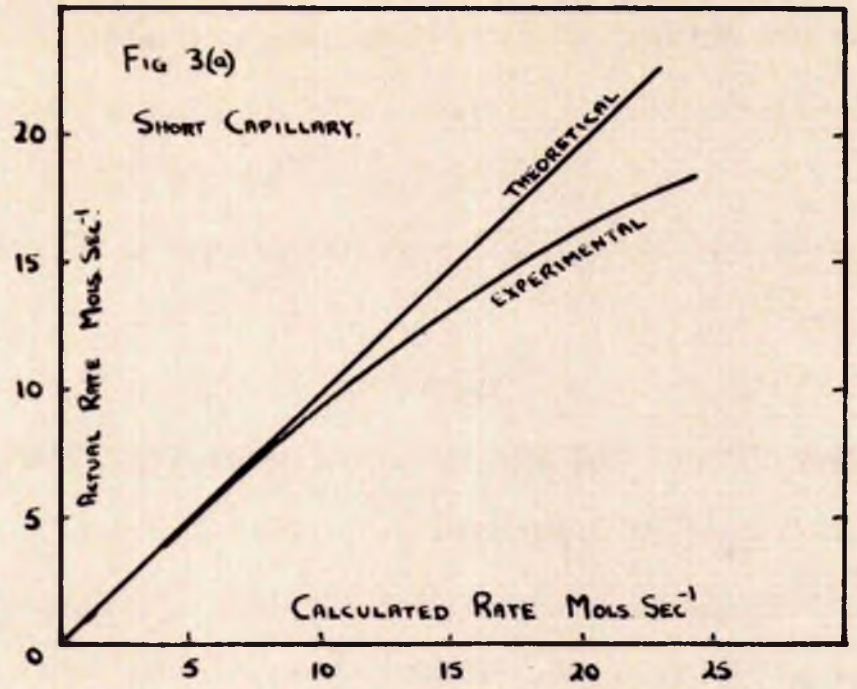
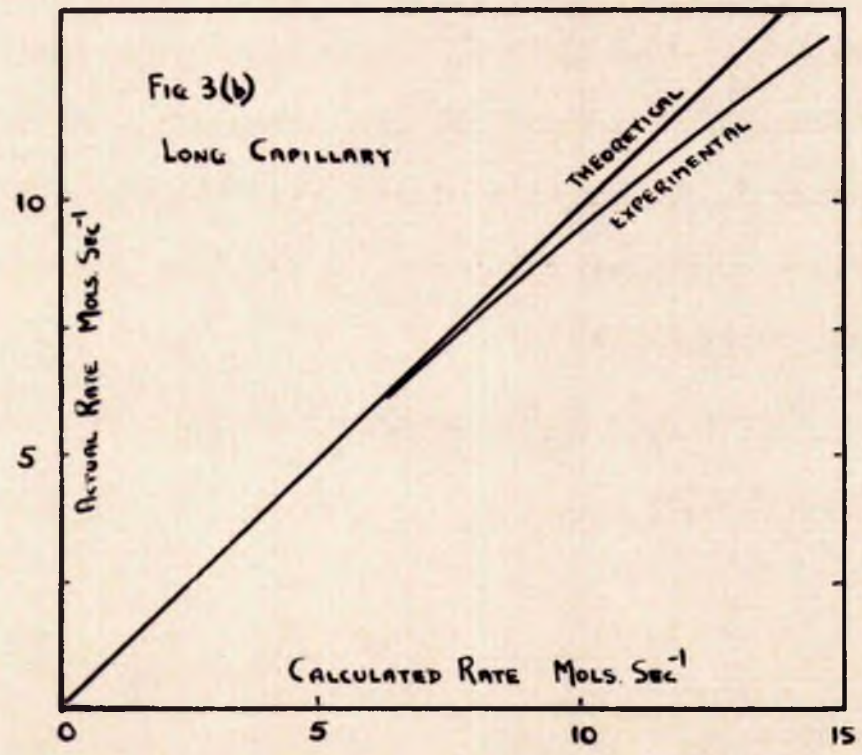


FIGURE 2

However, the experience of previous workers in St. Andrews[5, 6, 58] has shown that deviations from Poisseuille's Law are significant, especially at high rates of flow. Accordingly, it was felt that the capillaries should be calibrated directly. This was done by passing a known volume of dry air through the capillaries and measuring P_a and P_b on the double McLeod gauge. The apparatus used for this purpose is shown in Figure 2.

A plot of moles/sec. of air calculated using Meyer's formula against moles/sec. calibrated by the above method is shown for each capillary in Figures 3 (a) and 3 (b). As can be seen from these graphs the deviations were greatest at high rates of flow and were greater for the short than for the long capillary. In view of the fact that the deviation was more pronounced in the case of the short capillary, it seems reasonable to assume that the deviation was primarily an 'end-effect'. The derivation of Meyer's formula requires that the length of capillary shall be very large by comparison with its radius and also that the radius shall be much larger than the mean free path of the molecules of the gas stream. Since both capillaries had the same radius and the mean free path remains constant, the deviation must be attributed to the fact that the lengths of the capillaries were not sufficiently large by comparison with their radii. Other possible causes of deviation have been examined by Cowan[66] who found that neither 'slip' at the capillary walls, the correction for which he found to be insignificant, nor turbulence of the flow, since the Reynold's Number was too low for streamline flow to become turbulent, could be used to explain the deviations.





Figs. 3(a) and 3(b) Capillary Deviations.

In addition to a knowledge of the rate of flow of gas through the furnace, the average total pressure in the furnace had to be measured before the time of contact could be calculated. This could not be done directly without exposing the mercury in the McLeod gauge to the gas stream while it still contained reactant molecules. Some calibration experiments were therefore carried out in which one of the pair of McLeod gauges was connected via a two-way tap to a point on the furnace side of the jet to prevent back diffusion (see Figure 4). Various pressures of nitrogen were circulated and P_a, P_b and P_f (the pressure in the furnace section) were measured at several different rates of flow. If there was no resistance to flow between the furnace and the flow capillaries, P_b and P_f should have been identical. This was not found to be the case and thus, if we assume a negligible resistance along the length of the furnace itself, the collection traps must have constituted a measurable resistance. Now the total rate of flow, in moles per sec., must be the same throughout the apparatus and we may write

$$K(P_f^2 - P_b^2) = K^1(P_b^2 - P_a^2)$$

assuming the trap system to act like a capillary of constant K^1. Therefore

$$P_f = P_b^2 + \frac{K^1}{K}(P_b^2 - P_a^2)$$

and $\frac{K^1}{K}$ was found by this series of experiments to be 1.09. This equation was found to hold for both capillaries and over a large range of rates of flow. Since P_b and P_a had to be measured in every experiment in order to determine the rate of flow, it was a simple

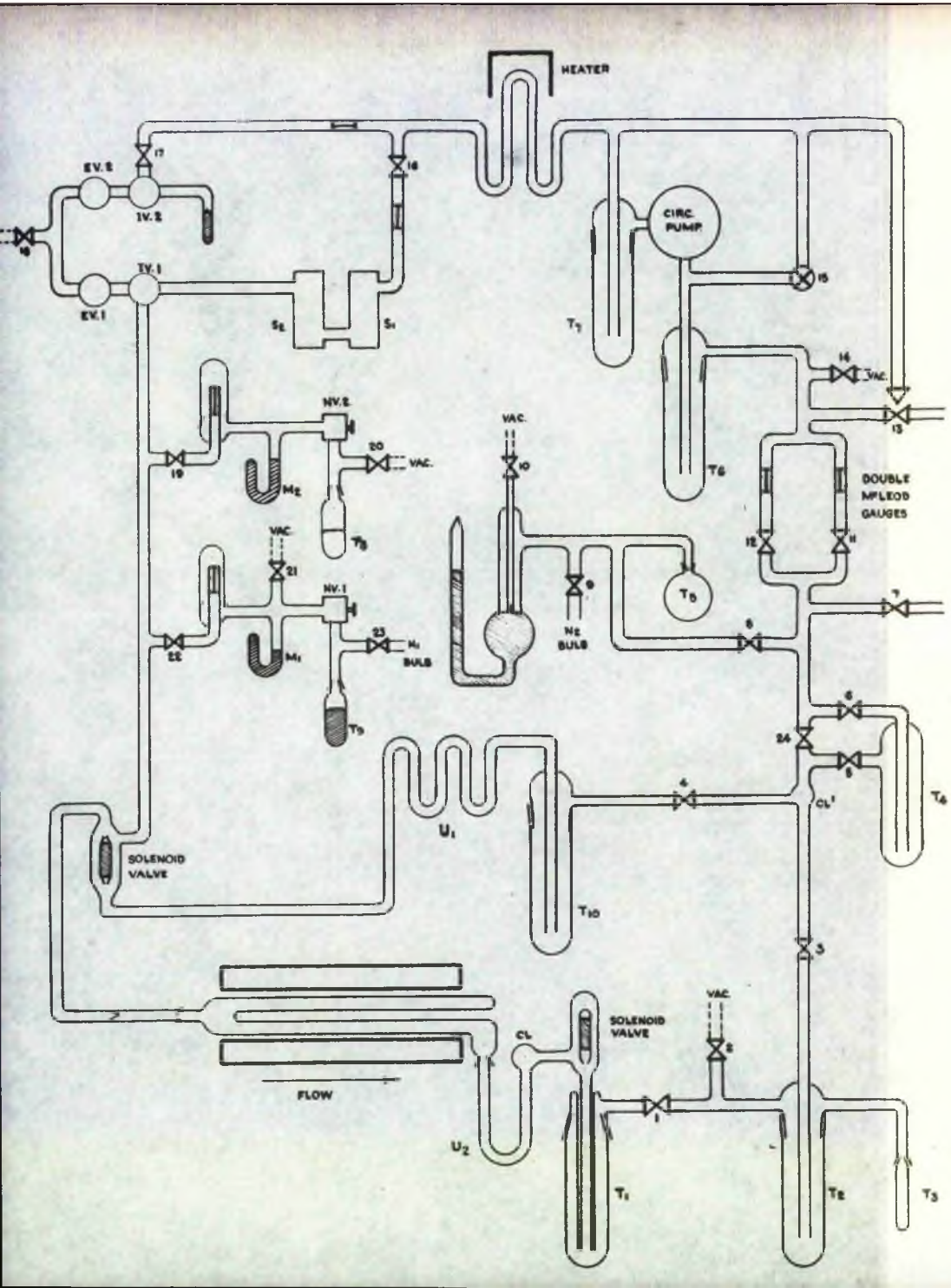

HEATER
EV. 2
IV. 2
17
16
EV. 1
IV. 1
S_2
S_1
CIRC. PUMP
15
T_7
14
VAC.
13
NV. 2
20
VAC.
19
M_2
T_8
VAC.
10
T_6
DOUBLE MCLEOD GAUGES
12
11
VAC.
21
NV. 1
9
T_5
7
22
M_1
23
H_1 BULB
N_2 BULB
8
6
24
5
4
CL'
T_4
U_1
SOLENOID VALVE
T_{10}
3
CL
SOLENOID VALVE
VAC.
2
FLOW
1
U_2
T_1
T_2
T_3

FIGURE 4

matter to calculate P_f from the same data.

REACTION VESSELS

Two reaction vessels were used in the course of the experiments, one of transparent silica, which was used in the major part of the work, and the other of pyrex. Both were fitted with a central thermocouple pocket. The volume of the silica vessel was 214 cc. and that of the pyrex vessel was 307 cc. The exit end of the pyrex vessel was detachable, by means of a ground glass joint which was sealed with picien wax. This permitted the introduction of pyrex tubes to alter the surface to volume ratio in a few experiments designed to study the effect of the surface on the reaction.

The vessels were heated by means of an electric furnace. This consisted of an inconel tube covered first with a layer of asbestos paper, then with a layer of alundum cement on which was wound nichrome tape. The nichrome tape was covered with a further layer of alundum cement and the whole encased in a two inch thick asbestos steam pipe casing. The winding had six tappings on it, including the two ends, and across these were connected shunting resistors. The shunts were adjusted so than an even temperature was produced in the working region and as sharp a fall as possible occurred at each end. The variation in temperature along the 'hot' length was ultimately reduced to $\pm$ 1.5°C. When the furnace had been so smoothed, the thermocouple was set in a position in its pocket which read the average temperature of the furnace.

A small auxiliary heater of nichrome tape was wound on to the

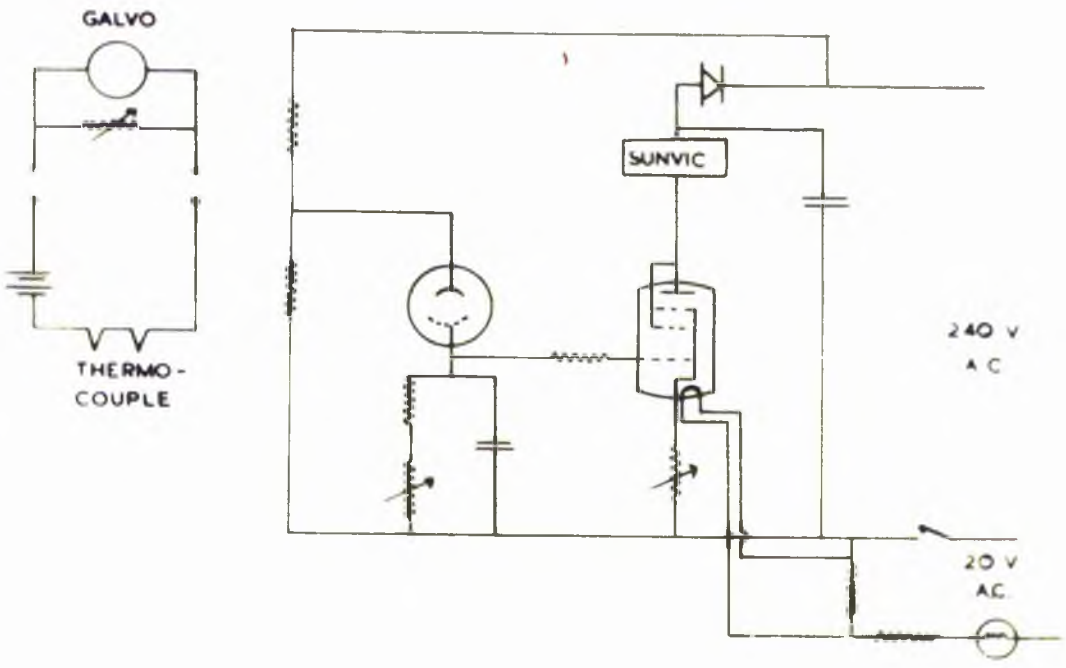


FIGURE 5

reaction vessels themselves and covered with asbestos paper. This was the heater which the furnace controller operated.

TEMPERATURE CONTROL AND MEASUREMENT

The main furnace heaters were supplied from the mains via a 500 watt voltage stabiliser and an auto transformer. Also included in the circuit was a rheostat to enable the main furnace current to be varied. This current was adjusted so that a temperature, somewhat below that required, was attained by the use of the main heaters alone. A furnace controller, modelled on that of Shepherdson[67], was used to switch the auxiliary heater on and off and so maintain the reaction vessel at a desired constant temperature. The circuit of the controller is shown in Figure 5. The E.M.F. generated by the thermocouple was balanced against that of the potentiometer. When the furnace was too hot the galvanometer light shone on the photocell and the negative voltage rose across the grid and cut off the valve. The Sunvic switch therefore opened and the auxiliary heater was switched off. Then the furnace cooled again and the light moved off the photocell, the negative grid potential fell, the valve again conducted, and the switch closed, switching on the auxiliary heater. In this way the temperature of the furnace could be controlled to within $\pm$ 0.5°C.

The temperature of the furnace was measured by means of a chromel-alumel thermocouple, the E.M.F. of which was measured on a direct reading potentiometer. The data of Roeser, Dahl and Gowens[68] was used to convert this E.M.F. to the corresponding

temperature in degrees Centigrade.

INJECTION SYSTEMS

The following compounds were all injected into the apparatus at some stage of the investigation, benzyl iodide, iodine, benzene, hydrogen iodide and methyl iodide.

(i) Benzyl Iodide Injection

The choice of the method of injection of a compound is governed mainly by the vapour pressure of the compound at some readily attained temperature and by the reactivity of the compound.

It was hoped initially that it would be possible to inject benzyl iodide through a capillary by means of some type of valve. In order to obtain a steady injection rate in this kind of system, a pressure of at least 20 mm. is required on the iodide reservoir side of the capillary. Although no accurate data are available on the vapour pressure of benzyl iodide it is reported by Whitmore and Thurman[69] to have a vapour pressure of ~10 mm. at about 95°C. It was therefore obvious that the iodide reservoir had to be maintained at a temperature in excess of 100°C and in order to prevent condensation on the valve it also had to be heated to more than 100°C. Previously much use had been made in St. Andrews of all metal bellows type valves which were connected to the apparatus by metal to glass seals. However, these valves were very prone to leaks in the bellows, especially when used at elevated temperatures and it was decided to look for a new type of valve.

A valve unit which operated by means of a pressed nickel

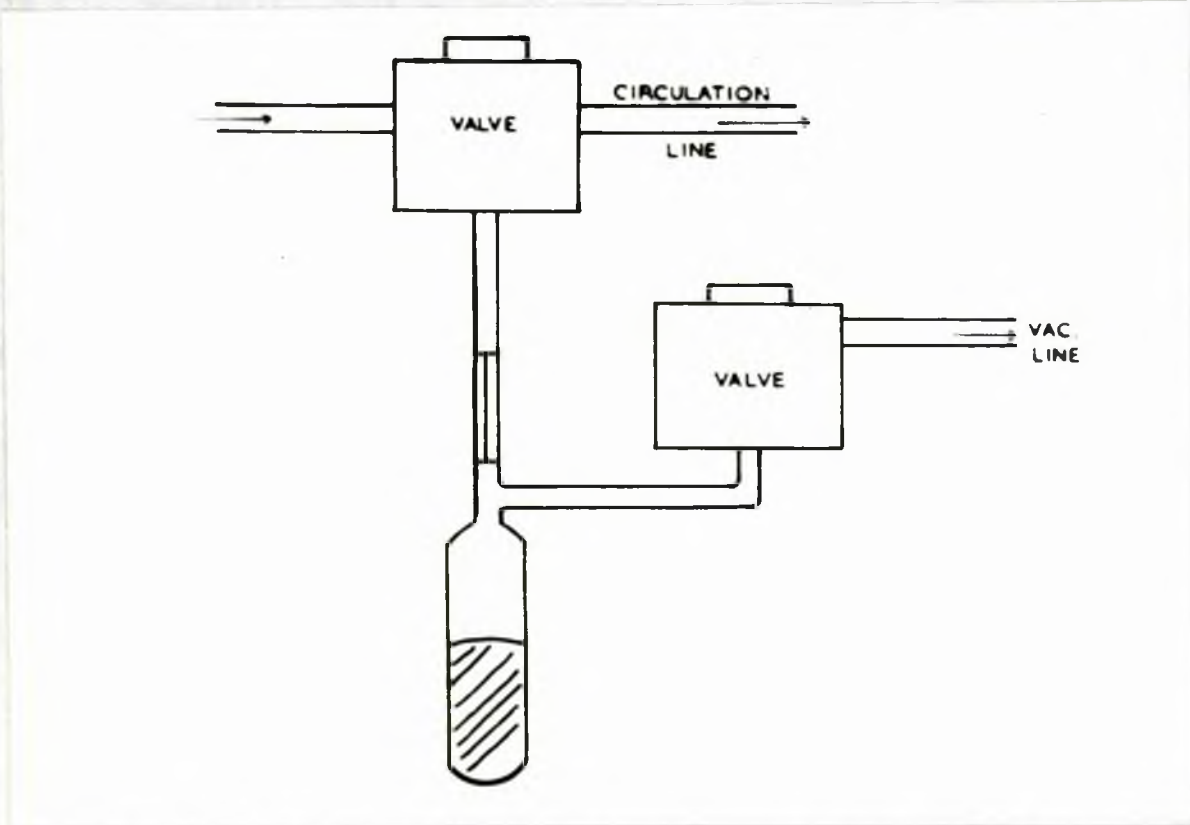
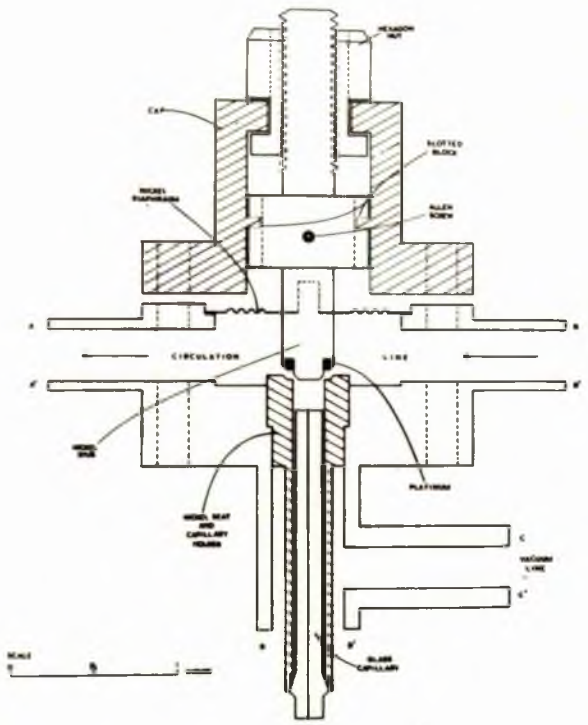


FIGURE 6



DIAPHRAGM VALVE

FIGURE 7

diaphragm was eventually designed. In practice two valves were needed when using a capillary injection method since it was necessary to evacuate the reservoir and outgas the iodide and it would be a very slow process to do this through the injection capillary. The system required is shown diagrammatically in Figure 6, and a scale drawing of the injection valve is shown in Figure 7. This type of valve operates by the thrusting of a rod of a soft metal into a machined seat of a harder metal, in this case the rod was platinum-tipped and the seat was made of nickel. This was found to give a very satisfactory valve action and trial injections of benzyl iodide were made. Unfortunately it was discovered that the iodide in contact with the hot valve (approximately 120°C) was rapidly decomposed. The cause of this was eventually traced to the silver solder used in constructing the valve, experiments having shown that the solder was an efficient catalyst for the decomposition of benzyl iodide. All attempts to poison this catalytic activity failed and it was decided that some means of injection which did not require the valve to be heated to such a high temperature would have to be employed. The method selected was the "saturator technique" - this consists of having a glass spiral, containing the compound, through which the carrier gas flows picking up the vapour pressure of the substance at the temperature of the spiral. Warhurst[70] showed that consistent injection rates were only obtained when two such saturators were employed, the first being maintained at about 10°C higher than the second controlling saturator, and this system was adopted. The valve unit, described above, was used as a "greaseless tap" to cut off the

saturators from the rest of the flow system. The way in which the saturators were linked to the rest of the system can be seen in Figure 4, which also shows the use of a "split-flow" technique to pick up the benzyl iodide in one section and the iodine or benzene in the other.

The temperature of the second saturator was maintained constant by means of a small water-filled bath, controlled by an Electro-Methods Cartridge thermostat. The bath had a small electrical heater immersed in the water and this was switched by the thermostat. Since temperatures in the region of room temperature were required, the bath also contained a copper coil through which cooling water could be circulated if the desired temperature lay a few degrees below room temperature. This constantly stirred water bath was capable of maintaining the temperature to within $\pm$ 0.1°C with ease. The first, or 'hot', saturator was kept at about 10°C above the second by surrounding it with a large Dewar vessel containing hot water at the appropriate temperature.

The main advantage which a saturator method of introducing a compound into the gas stream has over the more positive valve injection method is that a constant partial pressure of the compound is obtained. If the flow line was not divided this partial pressure would be the vapour pressure of the compound at the temperature of the saturator but, where a split-flow technique is used, it is a fixed fraction of this vapour pressure. Therefore a plot of the logarithm of the partial pressure of benzyl iodide injected by the

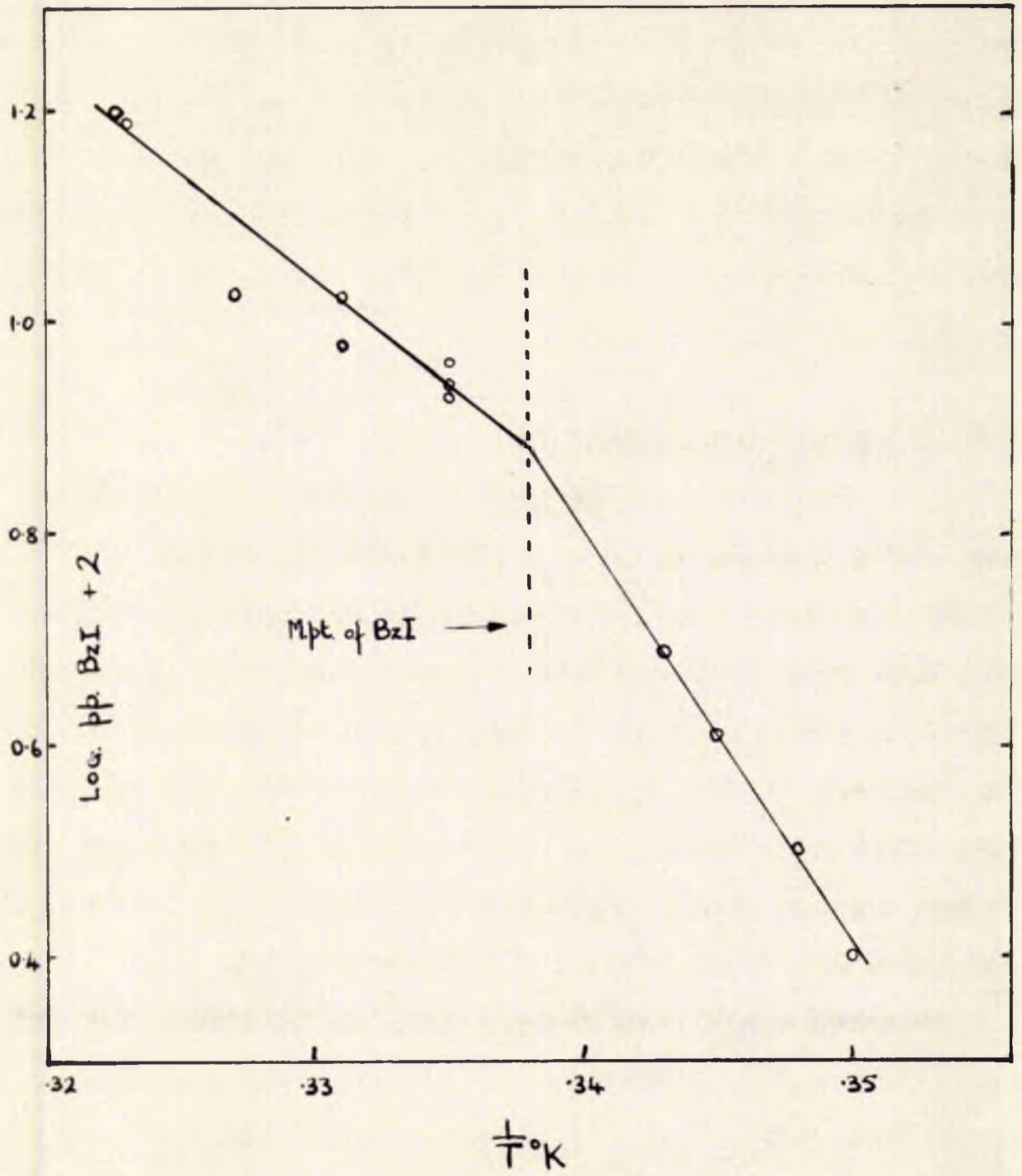


FIG. 8. LOG. OF BzI PARTIAL PRESSURE .V. $\frac{1}{T°K}$

system described above against the reciprocal of the temperature of the thermostat should be a straight line or rather two straight lines, since the temperature range covered includes the melting point of benzyl iodide. Figure 8 shows that this is in fact the case, the data all being obtained from runs where only benzyl iodide was injected, since the introduction of other compounds in significant amounts invalidates the above argument.

(ii) Iodine and Benzene Injection

Fortunately all the work in the design of the diaphragm type valves described in the previous section was not wasted as valves of this type proved highly satisfactory for the injection of iodine and at a later stage in the investigation these same valves were readily adapted to inject benzene. The main body of the valve, as well as the diaphragm, was made of nickel and the soft metal used was platinum, both nickel and platinum being highly resistant to iodine vapour even at high temperatures. A glass injection capillary was used and this was sealed into its nickel holder by silver chloride.

To obtain a sufficient vapour pressure in the iodine reservoir, it had to be heated to 80° - 100°C. This was done by means of a small, constantly stirred, oil-filled bath which was controlled to within $\pm$ .25°C by means of a Sunvic bimetallic steam thermostat. The bath had two heaters, the main one wound on the outside and an auxiliary one immersed in the oil and controlled by the Sunvic thermostat.

When in use, the valves were heated to about 30°C above the

reservoir temperature to prevent condensation of the iodine in the interior of the valve.

The only modifications required to make the valves suitable for the injection of large amounts of benzene were the replacing of the capillary by a much wider one and the provision of another thermostat which operated in the region 20 - 40°C. This thermostat was essentially the same as that used in the injection of benzyl iodide, the only difference being that a Fenwal thermostat was used instead of an Electro-Methods unit.

(iii) Hydrogen Iodide Injection

The vapour pressure of hydrogen iodide at the temperature of an acetone/solid carbon dioxide mixture is about 55 mm.[71] and this provides sufficient backing pressure for a simple capillary injection system. The apparatus used can be seen in Figure 4. Hydrogen iodide was frozen down into the small reservoir (T9) from the main storage bulb which was of five litres capacity and was painted black to prevent the slow photo-decomposition of hydrogen iodide. The small reservoir was then surrounded by acetone/solid CO_2 and the vapour passed through an Edwards needle valve, and then through the injection capillary into the main flow line. A mercury monometer, placed between the valve and the capillary, enabled the fore pressure of HI to be measured. Any desired fore pressure up to 55 mm. could then be obtained by adjusting the needle valve. Since a wide range of hydrogen iodide injection rates was required, it was found necessary to use several capillaries and these were therefore made

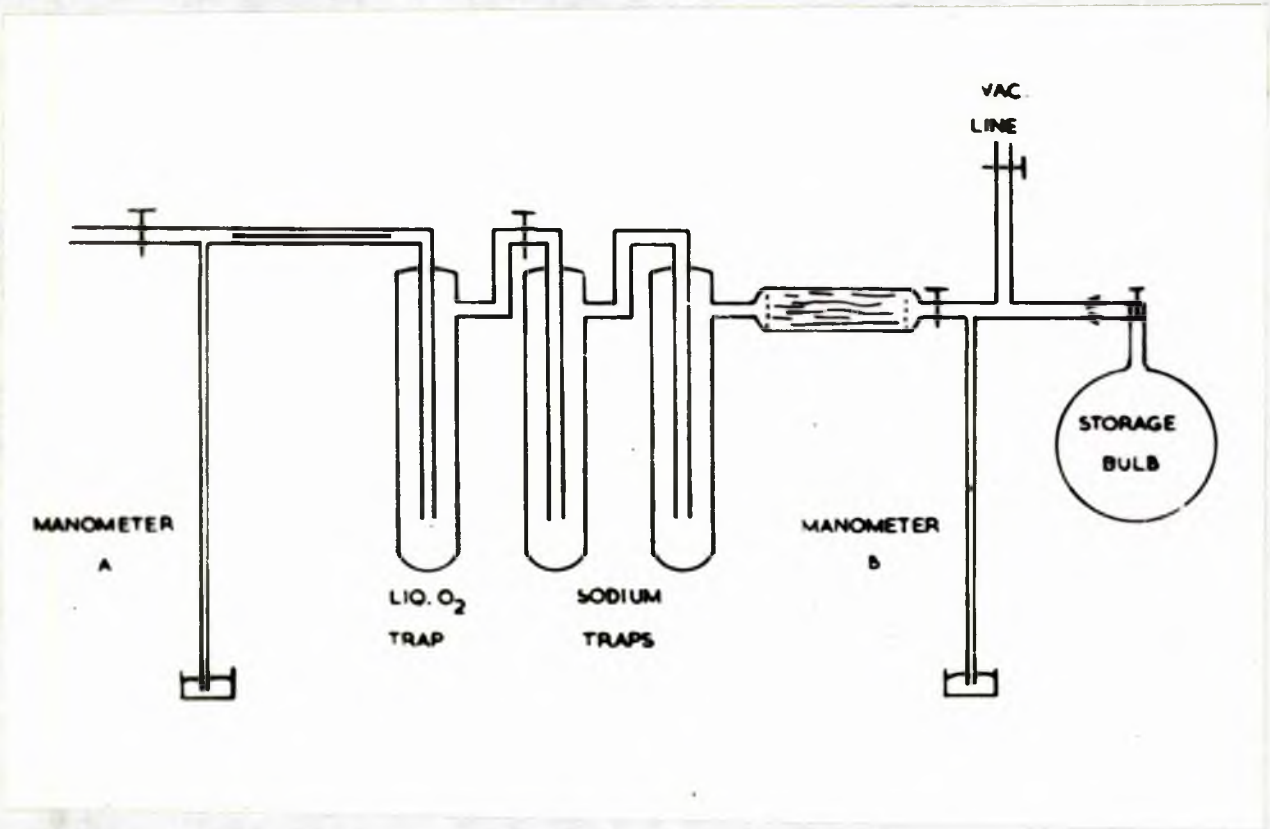

VAC.
LINE
STORAGE
BULB
MANOMETER
A
LIQ. O_2
TRAP
SODIUM
TRAPS
MANOMETER
B

FIGURE 9

interchangeable by the use of a B7 Quickfit cone and socket.

(iv) Methyl Iodide Injection

Methyl iodide has a vapour pressure of 141 mm. at 0°C[72] and thus it can conveniently be injected by a method similar to that just described for the injection of hydrogen iodide. The apparatus used can be seen in Figure 4. The methyl iodide was placed in the detachable reservoir (T8) and was thoroughly degassed before use.

PREPARATION AND PURIFICATION OF REAGENTS

(i) Nitrogen

The nitrogen carrier gas used in all of the flow experiments was carefully purified. The purification system, which was evacuated to approximately 10^{-5}mm. before use, is shown in Figure 9. B.O.C. cylinder nitrogen was passed through a fine capillary into a trap, which was cooled to -180°C to remove any condensable gases. It was then passed through two traps in series which contained sodium (the trap being heated externally by two small electric heaters) to remove any oxygen present. A tube packed with glass wool prevented any sodium oxide being carried through with the gas stream which then passed into the storage bulb, monometer B being provided to measure the pressure in the storage volume.

(ii) Benzyl Iodide

The method used for the preparation of benzyl iodide was that of Norris[73], as modified by Gazith and Noyes[23]. Basically,

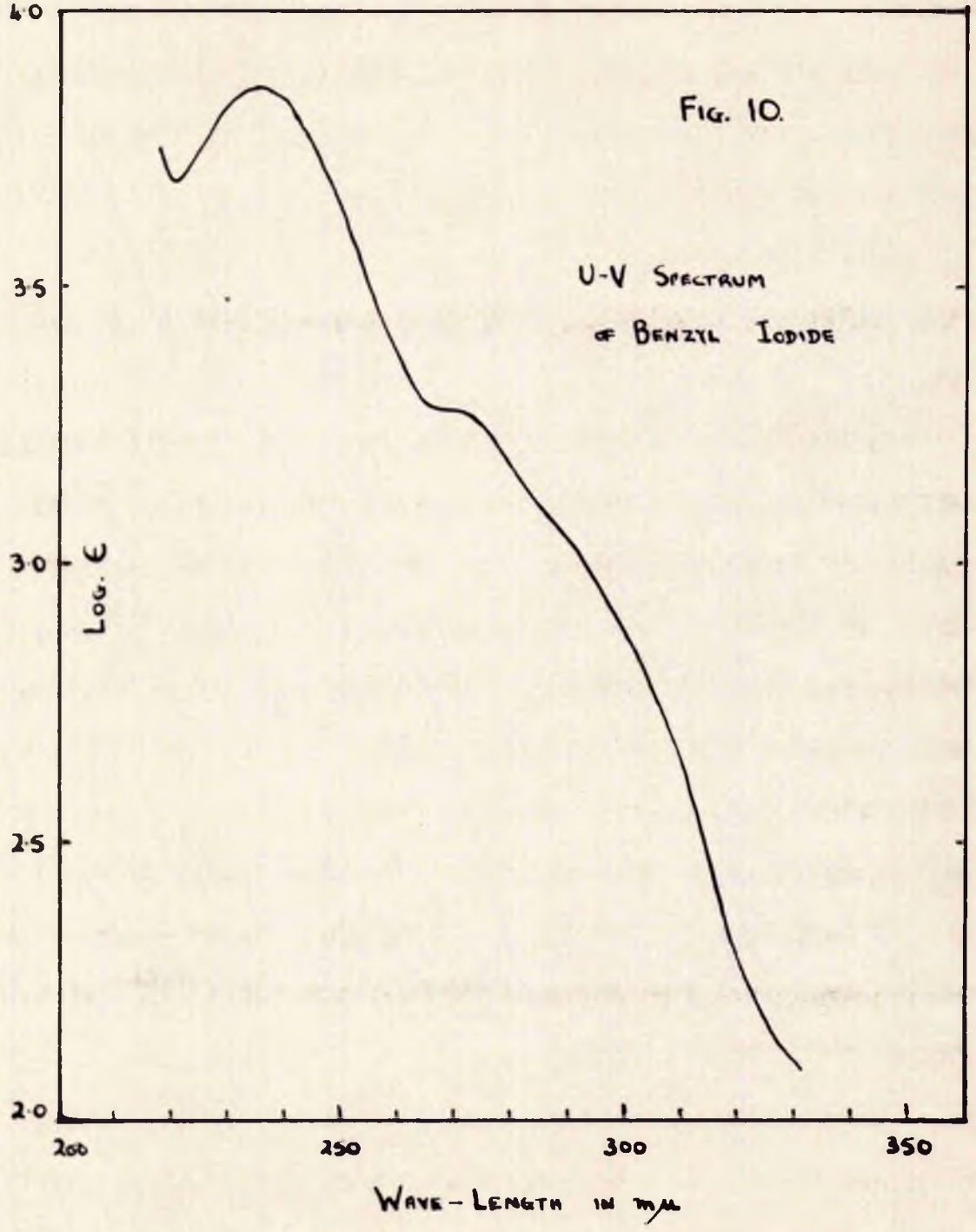


Fig 10. Log. of Molar Extinction Coefficient .V. Wave-Length

the method consisted of reacting benzyl alcohol with concentrated hydriodic acid, a good yield of the iodide being obtained in the presence of an excess of acid. In practice, about 50 cc. of benzyl alcohol and 200 cc. of commercial hydiodic acid (which contained some free iodine) were shaken for about five hours. Two layers were formed and the lower oily layer was separated off. This was washed with sodium bisulphite solution (to remove free iodine) and solid benzyl iodide was obtained. The iodide was filtered off and vacuum dried.

Purification by recrystallisation proved to be difficult and rather wasteful, as did distillation under reduced pressure as suggested by Gasith and Noyes[23]. The substance was therefore purified by sublimation at low pressures. The benzyl iodide, thus obtained, was a white crystalline solid which melted at 23.5°C. As a check on the purity of the benzyl iodide produced in this way, its U-V adsorption was measured over the range 220 mμ to 340 mμ . The resulting spectrum is shown in Figure 10 which shows maxima at 270 mμ (log ϵ = 3.28) and 235 mμ (log ϵ = 3.86). These values are in excellent agreement with those of Hillmer and Paersh[74] who quote maxima at 270 - 274 mμ (log ϵ = 3.3) and at 238 - 235 mμ (log ϵ = 3.9). Their spectrum does not show the decline in the extinction coefficient at wave lengths less than 235 mμ but this is probable due to the fact that they made very few observations at wave lengths less than 250 mμ .

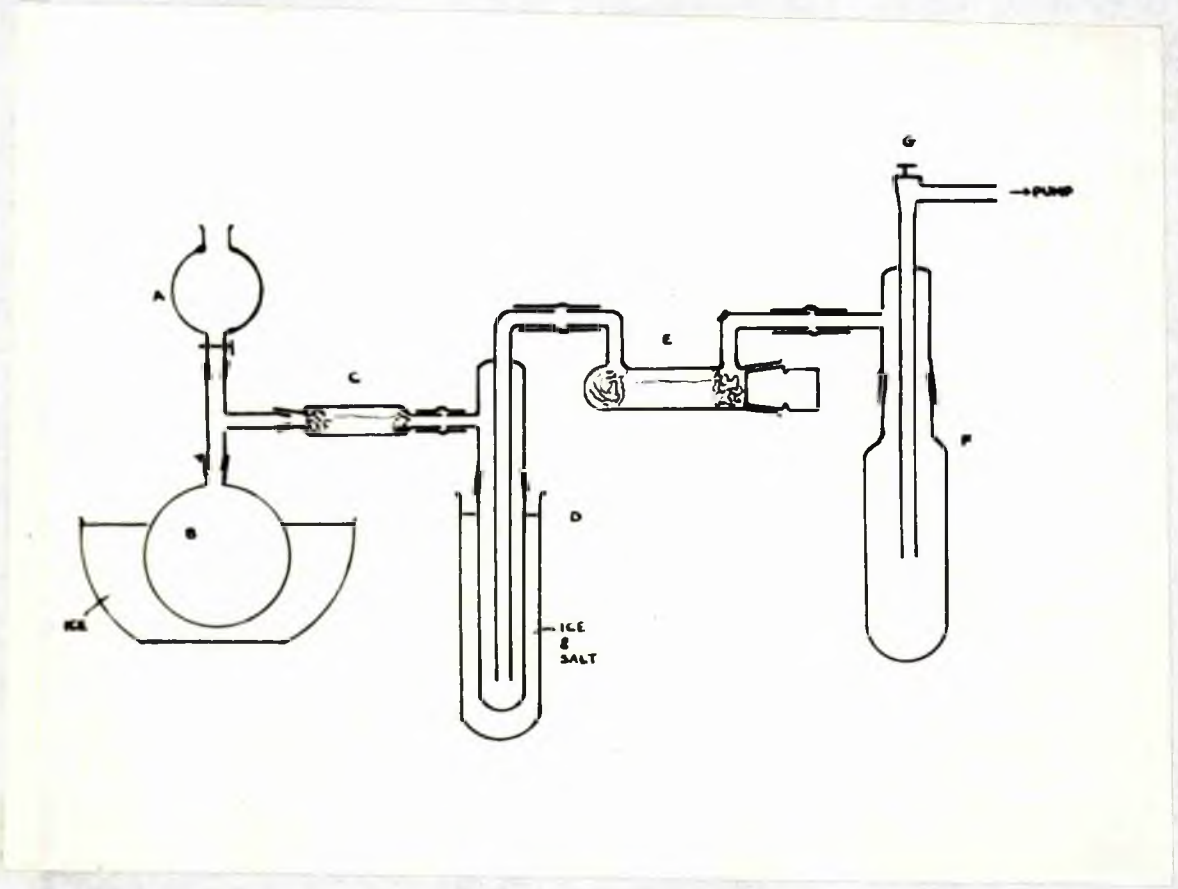


FIGURE 11

(iii) Hydrogen Iodide

Pure hydrogen iodide, required for use as a radical acceptor, was prepared as shown in Figure 11. Commercial 55% hydriodic acid contained in the dropping funnel (A) was allowed to drop slowly into phosphorus pentoxide in the flask (B). The phosphorus pentoxide absorbed the water and gaseous hydrogen iodide was drawn through the purification apparatus by means of a water pump. The purification apparatus consisted of two tubes (C) and (E) containing more phosphorus pentoxide to remove traces of moisture and a trap (D), cooled in a mixture of ice and salt, to remove free iodine. The product was collected in trap (F) which was cooled in liquid oxygen. The reaction vessel (B) tended to heat up during the reaction and so it was surrounded by an ice bath.

The product still contained a certain amount of free iodine and was further purified by bulb to bulb distillations at low pressures - distillation being from a trap cooled to -80°C in an acetone/solid carbon dioxide bath to a trap cooled in liquid oxygen - and then distilled into the hydrogen iodide storage bulb.

(iv) Iodine

A resublimed grade of commercial iodine was given a further sublimation before use.

(v) Benzene

"Analar" grade benzene was used without further purification.

(vi) Methyl Iodide

Methyl iodide was distilled using a short "Fenske" column and the fraction boiling between 42 - 43°C was collected. This had a faint pink colour due to traces of free iodine. The colour was removed by shaking with a small amount of mercury.

COLLECTION SYSTEM

A triplicate system of collection traps was used in order to check the constancy of the results being obtained. In Figure 4 of the whole apparatus, the collection system is connected to the points CL and CL^1. The gas stream after leaving the furnace could pass through any one of four solenoid valves, three leading to the analysis system and one to a spare trap which was used when stabilising conditions of flow, rates of injection etc. The solenoid valves consisted of a metal rod, sealed inside a glass tube carrying a B 14 standard cone, which could be raised or lowered into the socket at the top of the trap by means of a solenoid magnet. Each collection system (of which only one is shown) consisted of three traps. The first (T1) had a double walled inlet tube and a nichrome tape heater was positioned between the walls so that the inlet tube could be heated without exposing the gas stream to the metal of the heater. The trap was so constructed to prevent the more involatile of the products from condensing out in the entrance tube and eventually blocking it. The trap was cooled to -80°C in acetone-carbon dioxide. Leaving T1, the gas stream next passed through an ordinary trap (T2) which was

cooled in liquid oxygen to remove the rest of the products, before rejoining the main recirculation system. On a side-arm of T2 was attached a small trap (T3) which contained degassed methanol. In the experiments using hydrogen iodide, the hydrogen iodide condensed out in T2 and was subsequently distilled into the methanol in T3. In addition to the system of collection traps a furnace by-pass system was included. The object of this system was to enable measurements of the amount of reactant being injected to be made. Obviously this could not be done after the reactant had passed through the furnace and therefore a by-pass valve, similar in type to the solenoid valve already mentioned, was inserted between the injection system and the furnace. By raising the glass cone in this valve, the gas stream was diverted through a double U-tube (U1), cooled to -80°C, and a trap T5 similar to the heater trap T1. The double U-tube was used to collect benzyl iodide, and the trap T5 to collect iodine, in those experiments where iodine was added.

DESCRIPTION OF AN EXPERIMENT

Since several kinds of experiment were performed with this apparatus, a general description of the technique of performing a run in which benzyl iodide and hydrogen iodide were injected, will be given first and a description of the various modifications given later. The diagram of the complete apparatus in Figure 4 is used to illustrate this section dealing with experimental procedures.

Pure methanol was placed in T3 and the other two corresponding

traps and the methanol frozen down in a liquid oxygen bath. About 1 gram of the purified benzyl iodide was placed in the primary saturator S1 and this was surrounded by a -80°C bath. All the taps except 9 and 23 were then opened to the vacuum line and the apparatus pumped down to 10^{-6} cm. or lower. When a satisfactory vacuum had been obtained, the system was isolated by closing taps 2, 10, 14, 18, 19, 20, 21 and 22. After closing taps 1 and 3, the methanol in T3 was allowed to warm up to room temperature, evolving some of the occluded air. The methanol was subsequently refrozen, tap 2 reopened to the vacuum line and the released air pumped out. This "degassing" procedure was repeated twice. A similar "degassing" of the benzyl iodide in S1 was carried out via EV1 and tap 18. By closing tap 8 and opening tap 9, nitrogen, from the reservoir, filled the manostat section, pushing the mercury down below the end of the inner tube of the manostat, the inner tube being closed with a carborundum disc which is porous to gases but not to mercury. Thus, when tap 9 was closed and tap 10 opened, nitrogen was pumped out until the mercury in the manostat sealed off the porous disc and a definite volume of nitrogen was contained between tap 8 and the disc. (T5 was an ordinary standard joint flask and was made interchangeable so that flasks of different volumes could be substituted and therefore different fixed volumes of nitrogen obtained). Tap 8 was opened and the nitrogen filled the circulation system of the apparatus (normally to a pressure of about 4 mm.). The solenoid valve controlling the entrance to the spare trap was then opened and the mercury diffusion pump started by

raising the hot bath around the bulb. Tap 24 was closed and taps 5 and 6 opened so that the nitrogen flowed through T4. This trap contained hot sodium which reacted with any traces of oxygen left in the nitrogen and converted it to sodium oxide. After circulating the nitrogen through T4 for about one hour, tap 24 was reopened and the sodium trap isolated. Hydrogen iodide from the storage reservoir was distilled into T9 which, after tap 23 had been closed, was surrounded by a -80°C bath. On opening tap 22, hydrogen iodide flowed into the nitrogen stream and its rate of injection could be controlled by use of N.V.I., the pressure before the capillary being measured on the manometer M1. The rate of flow of nitrogen plus hydrogen iodide was measured using the double McLeod gauges and if necessary the rate was adjusted by means of the by-pass tap 15. A satisfactory rate of flow having been obtained, the -80°C bath on S1 was removed and replaced by a water bath about 10°C hotter than the thermostatted bath on S2 and the injection valve IV1 was opened. Benzyl iodide now flowed into the system at a rate which was governed by the setting of the thermostat surrounding S2 and by the rate of flow of nitrogen. When all the injection rates became steady and the temperature inside the reaction vessel was at the desired value, the flow was switched from the spare trap to the first analysis system. Undecomposed benzyl iodide and iodine appeared in T1 and the unchanged hydrogen iodide and toluene in T2. The flow was continued through this system for a known time, usually between 15 and 30 minutes, depending on the quantities of iodide being injected. This was repeated for the second and third analysis systems. The hydrogen iodide injection was then stopped

while the gas again flowed into the spare trap. When the flow had restabilised, usually after 5 minutes, the by-pass solenoid valve was raised and benzyl iodide was collected in the double U-tube U1 which was cooled to -80°C. (A double U-tube was used to ensure complete removal of the iodide from the gas stream). Finally the flow was again switched to the spare trap and the benzyl iodide injection valve closed. After a few minutes, the circulation pump was switched off and the hydrogen iodide and toluene in T2 were distilled into the small trap T3. This was done by closing taps 1 and 3 and opening 2 and pumping out the section to approximately 10^{-5} cm. Tap 2 was then closed and the liquid oxygen bath removed from T2. The hydrogen iodide and toluene distilled over into T3 and were frozen down onto the surface of the solid methanol. T3 was then allowed to warm up and the methanol dissolved the products. After refreezing, T3 was pulled off, filled up quickly with more methanol and the contents analysed. Air was then admitted to the rest of the circulation system and trap T1 (and the other two corresponding traps) removed. The products in these traps were dissolved in methanol, great care being taken to ensure that none of the product was left adhering to the inner tube of the trap, and made up to standard volumes for analysis. The benzyl iodide in U1 was also dissolved in methanol after the U-tube had been cut from the apparatus.

It was found that the benzyl iodide, left in S2 after an experiment, slowly decomposed and this was undesirable as it could lead to the injection of iodine along with the benzyl iodide in the next experiment. Therefore, after every experiment, S1 was replaced by a simple U-tube

surrounded by a -80°C bath. Tap 16 was closed and the saturator section pumped out via EV1 and tap 18. The residual benzyl iodide in S2 was then allowed to distil into the U-tube and was discarded before the next experiment was started.

In experiments in which iodine was injected, the amount being injected was calibrated by use of T10. This calibration was performed before the experiment proper was started. With tap 16 closed the nitrogen flow was no longer split and all of the nitrogen flowed through IV2. When T11 was surrounded by its oil thermostat at a given temperature, the amount of iodine injected was independent of the rate of flow through IV2 and therefore was the same whether tap 16 was open or closed. Thus, by opening the by-pass valve, while T10 was at -80°C and U1 was at room temperature, the rate of injection of iodine could be measured by collecting the iodine in T10 for a known time. Similarly in experiments in which benzene or methyl iodide was used, the injection rate was calibrated prior to the main experiment. In these cases, however, the by-pass system could not be used as it did not have a suitable collection trap and so one of the collection system sections was used for the calibration. Benzene and methyl iodide were both unaffected by passage through the furnace at the temperatures involved and were collected in T2. They were ultimately distilled into T3 which, in such cases, contained no methanol.

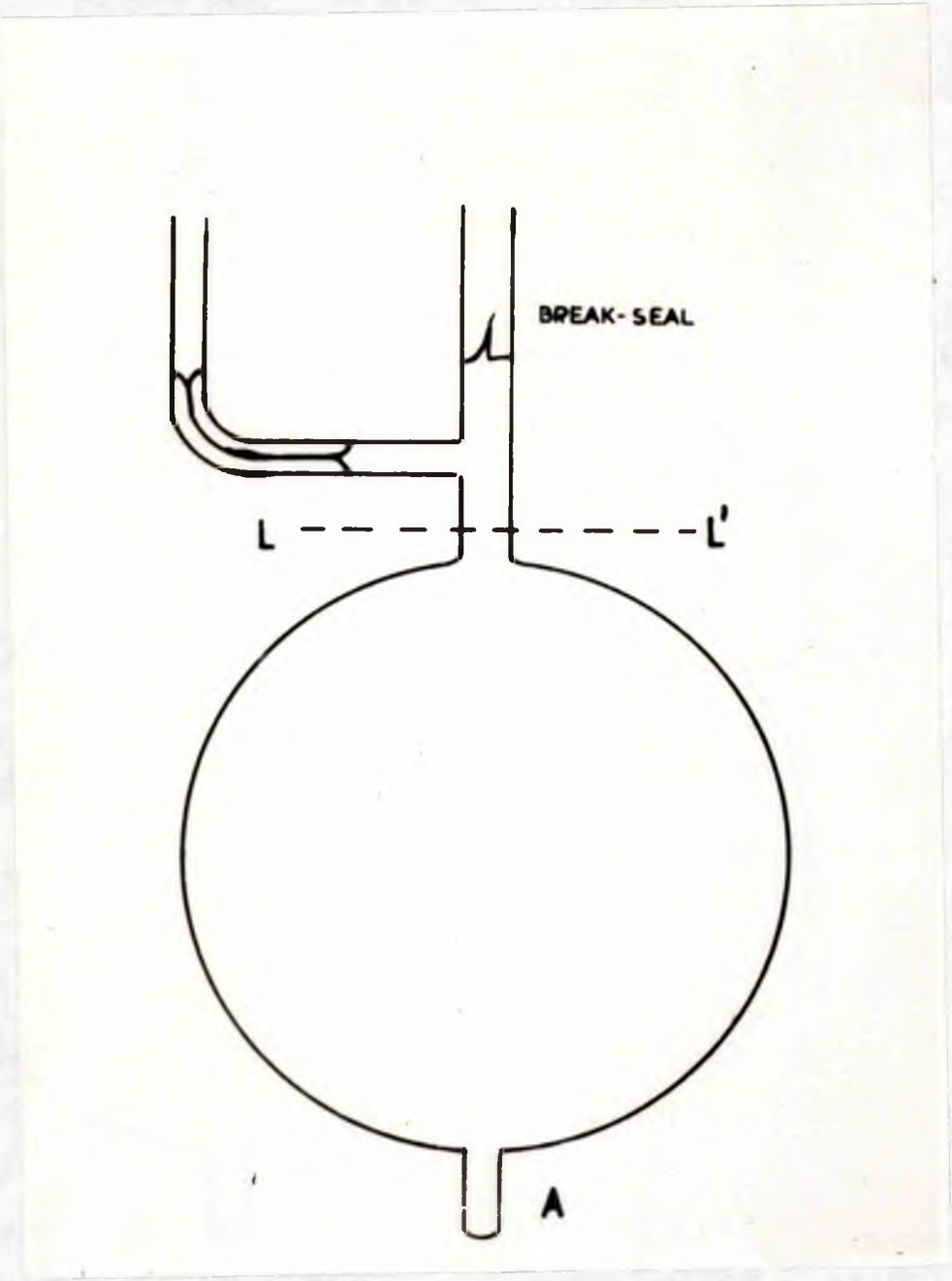


FIGURE 12

(b) STATIC METHOD

The apparatus used in the static system was much simpler than that used in the flow method. In essence the method consisted of placing a sealed bulb, fitted with a break-seal, in a furance at a controlled temperature for a known period of time.

The type of reaction vessel used is shown in Figure 12. The part of the vessel above LL^1 was made as a unit and replaced after each experiment. The majority of the experiments, performed in the static system, were studies of the decomposition of benzyl iodide alone. A weighed amount of benzyl iodide in a small sample tube was carefully placed in the tube A (Figure 12) at the bottom of the reaction bulb and the sealing-off unit was then glass blown on. The vessel was attached to the vacuum line and evacuated through the capillary constriction. During evacuation the tube A was surrounded by a -180°C bath to prevent any of the benzyl iodide being pumped off. When a pressure of 10^{-5} cm. or less had been obtained the vessel was sealed off and inserted into the furnace. This furnace was of the same type as that used in the flow system, except that, in this case, the temperature was controlled to within $\pm$ 0.5°C by a commercial Sunvic controller. This type of controller operates by having a platinum resistance thermometer placed in the furnace; this thermometer and the normal thermocouple being fixed co-axially in the furnace. The main defect of this system was that, when the furnace was opened to introduce the reaction vessel, the temperature fell considerably and it took a few minutes for the controller to bring the temperature back

to its desired value. This made the time of starting the reaction uncertain. Nevertheless this error was not serious if the total time of reaction was long and, in these experiments, a reaction time of at least two hours was used, whenever possible, in order to minimise the errors due to the uncertain time of starting. After the desired reaction time had elapsed, the vessel was removed and the tube A cooled in a -80°C bath in order to rapidly quench the reaction. A standard B.14 joint was then attached to the break-seal and the reaction vessel unit connected to a vacuum system via a system of collection traps which was identical with one of the analysis trap systems on the flow apparatus. When a satisfactory vacuum had been obtained in the trap system, the tap to the vacuum line was closed and the seal broken. The products of the reaction were allowed to distil out of the reaction vessel into the collection traps, the method of collection being exactly the same as that used in the experiments with the flow system.

A few experiments, in a static system, were also made on the decomposition of the iodide in the presence of hydrogen iodide. This reaction is much faster than the reaction without the radical acceptor and, therefore, a much lower temperature was required. The technique used was similar to that above, except that a large oil-filled thermostat (instead of the furnace) was used to heat the reaction vessel. The thermostat consisted of a well lagged 1 gallon iron tank which was fitted with an ordinary 1500 Watt kettle heater near the base. The heater was fed from the mains through an auto-transformer with a rheostat in series with it so that the main heater current could be

varied. A small coiled-wire heater, of approximately 40 ohms resistence, was also included and this was controlled by a Sunvic stem thermostat. The oil in the thermostat was constantly stirred by a small impeller type stirrer and the temperature distribution throughout the bath was very uniform. This thermostat was capable of maintaining the temperature to within 0.25°C over very long periods of time. This method of heating had the advantage over the electric furnace of having a much higher heat capacity and was thus not appreciably cooled by the insertion of the reaction vessel.

(c) ANALYTICAL TECHNIQUES

Many analytical methods were used in this investigation and a discussion of each, as applied to the various reactants and products, is given below.

FREE IODINE

Small quantities of free iodine were obtained in the decomposition of benzyl iodide and these were removed from the apparatus as a solution in methanol. The iodine concentration in these solutions was often 10^{-3} molar or less and thus a sensitive method of analysis was required. The normal starch detection of the end-point in thiosulphate-iodine titrations, while being very sensitive, is liable to error if the iodine solution is made up in more than about 20% alcohol. The starch end-point is also rather difficult to observe when titrating with 10^{-3} N thiosulphate. The technique selected was the amperometric method of Foulk and Bawden[75] in which two platinum electrodes are placed in the solution containing the iodine and a 10 mV potential is applied to them. The current flowing in the circuit is measured by means of a sensitive galvanometer. As thiosulphate is added, the current gradually diminishes and reaches zero at the end-point of the titration. The 10 mV required was supplied from a Pye Potentiometer and the galvanometer used was a Tinsley, which had a scale sensitivity of 1650 mm. per micro-amp. According to Potter and White[76], this method is accurate to 0.01 ml. of 10^{-4} N thiosulphate if the galvanometer sensitivity is greater than 1500 mm. per micro-amp.

The method was found to be very satisfactory for use in titrations with 10^{-3} N thiosulphate and to be unaffected by the presence of methanol.

BENZYL IODIDE

Two methods were available for the determination of benzyl iodide. These were (a) hydrolysis with sodium hydroxide solution and subsequent estimation of the sodium iodide with silver nitrate and (b) displacement of the iodine by bromine followed by its oxidation by free bromine to the iodate and estimation of iodine liberated on addition of potassium iodide. The second method was selected because it could also be applied to the other iodides used in the investigation viz. hydrogen iodide and methyl iodide.

This oxidation by free bromine method is essentially that of Pregl[77] for the analysis of methyl iodide in Zeisel determinations. 10 ml. of the iodide solution and 10 ml. of a 10% solution of sodium acetate in glacial acetic acid are placed in a 250 ml. conical flask, fitted with a ground glass stopper. About five drops of "Analar" bromine are added, followed by 25 ml. of a 20% aqueous solution of sodium acetate and the mixture placed in the dark for approximately one hour. Excess bromine is then removed by addition of "Analar" formic acid until the solution is colourless and no longer decolourises methyl red. The addition of 10 ml. of 10% potassium iodide solution and 25 ml. of 2 N sulphuric acid liberates free iodine and this can be titrated with 10^{-2} N thiosulphate, using a starch end-point.

HYDROGEN IODIDE

The hydrogen iodide, which was removed from the apparatus as a solution in methanol, was made up to a standard volume with water. Estimation of the iodide was then carried out in a similar manner to that described for benzyl iodide. However, since much larger amounts of hydrogen iodide were being used, more bromine had to be added to ensure complete oxidation and the liberated iodine was titrated with 10^{-1} N instead of 10^{-2} N thiosulphate.

METHYL IODIDE

The methyl iodide, which is the compound for which the Pregl method[77] was originally developed, was also estimated by bromine oxidation.

BENZENE

A few experiments were performed in which benzene was passed through the reaction vessel along with the benzyl iodide and hydrogen iodide. In these instances, one of the three collection systems was used to measure the amount of benzene being injected. This was done by shutting off the benzyl iodide and hydrogen iodide injection units and allowing the benzene to be collected in the trap cooled in liquid oxygen. At the end of the experiment, the benzene was distilled into the small trap (T3) (which, in this case, contained no methanol) and estimated gravimetrically.

The analytical methods described in the foregoing paragraphs were used as a routine procedure after every experiment to which they were

applicable. Other methods of analysis, including mass spectrometry, U-V Spectrophotometry and I-R Spectrophotometry were also used. They were, however, only employed on specific occasions and they will be described in their correct context in the following section of the thesis which deals with the experimental results.

EXPERIMENTAL RESULTS

AND DISCUSSION

EXPERIMENTAL RESULTS AND DISCUSSION

In a previous study of the decomposition of benzyl iodide by Szwarc[1], it was shown that the products of the decomposition were dibenzyl and iodine, although no evidence for the equivalence of these products was presented. The investigation also showed that, although the reaction was independent of the surface of the reaction vessel, the decomposition was not a simple first order reaction and it was suggested that the dissociation, envisaged as the first step, was partially reversible. The first part of the present investigation was devoted to attempts to establish the nature of this reverse reaction and, if possible, to derive a bond energy for the carbon-iodine bond in benzyl iodide. The possibility of eliminating the reverse reaction by the use of hydrogen iodide as a radical acceptor was examined in the later sections of this work. (A complete record of all the primary experimental data, viz. temperatures, concentrations, percentages of decomposition, reaction times etc., is given in the tables in Appendix 1).

1. THE SYSTEMS BENZYL IODIDE ALONE AND BENZYL IODIDE PLUS FREE IODINE

1.1 EXPERIMENTS USING A FLOW SYSTEM

The first step in the present investigation was to try to establish that the overall reaction, which takes place when benzyl iodide decomposes, is $2\ BzI \longrightarrow Bz-Bz + I_2$. It was decided to attempt to determine by mass spectrometry the amount of dibenzyl formed in the reaction. Unfortunately it proved impossible, in the course of a normal experiment, to separate benzyl iodide, iodine and dibenzyl as they left the reaction zone and they were all collected in a trap, cooled with an acetone/solid carbon dioxide mixture. All the products were subsequently dissolved in pure methanol and aliquots of this solution used for iodine analyses in the usual way. A further quantity of this solution was shaken with mercury (to remove free iodine), filtered, and then the solvent was removed by distillation under vacuum from an ice bath to a trap at -20°C. It was shown, by using known solutions of benzyl iodide and dibenzyl in methanol, that this distillation procedure did not result in any detectable amount of dibenzyl being distilled off, although a considerable amount of benzyl iodide was removed. (It was estimated that the vapour pressure of benzyl iodide is about 100 times that of dibenzyl at 0°C). The residual solids were vaporised in a heated solids handling system and injected into a Nier type mass spectrometer.

Before the mass spectrometer could be used to give quantitative dibenzyl analyses, it was necessary to calibrate the instrument by

the injection of known amounts of dibenzyl. In order to allow for variations in the sensitivity of the instrument, the peak heights corresponding to mass 182 (i.e. dibenzyl) were always corrected to a fixed sensitivity - the sensitivity being determined by the peak corresponding to mass 40 given by a known pressure of argon. The response of the instrument to dibenzyl was shown to be linear provided that sufficient time (about 15 minutes) was allowed to elapse between the injection of the solid and the measurement of the peak height. The sensitivity of the mass spectrometer was 6.95 mV/mgm. of dibenzyl at an argon sensitivity of 2 V/mm.

As a check on the accuracy of the overall technique, 2.93 mgm. of pure dibenzyl were dissolved in 100 cc. of methanol and the solvent removed by the distillation process described above. A mass spectrometer analysis of the residual solid showed it to be equivalent to 2.99 mgm. of dibenzyl - an error of approximately 2%. This process was repeated several times and the divergence between the actual amount of dibenzyl used and the amount found varied between 0.5% and 2% in either direction.

This method was employed in three experiments to determine whether the amount of iodine and of dibenzyl being produced from benzyl iodide were, in fact, equivalent. The results are shown in Table 3. It is evident from the table, that although the rate of formation of dibenzyl is very close to the rate of formation of iodine, it was, in all three instances, slightly lower. For this reason, attempts were made to identify any other possible products which might have been formed from

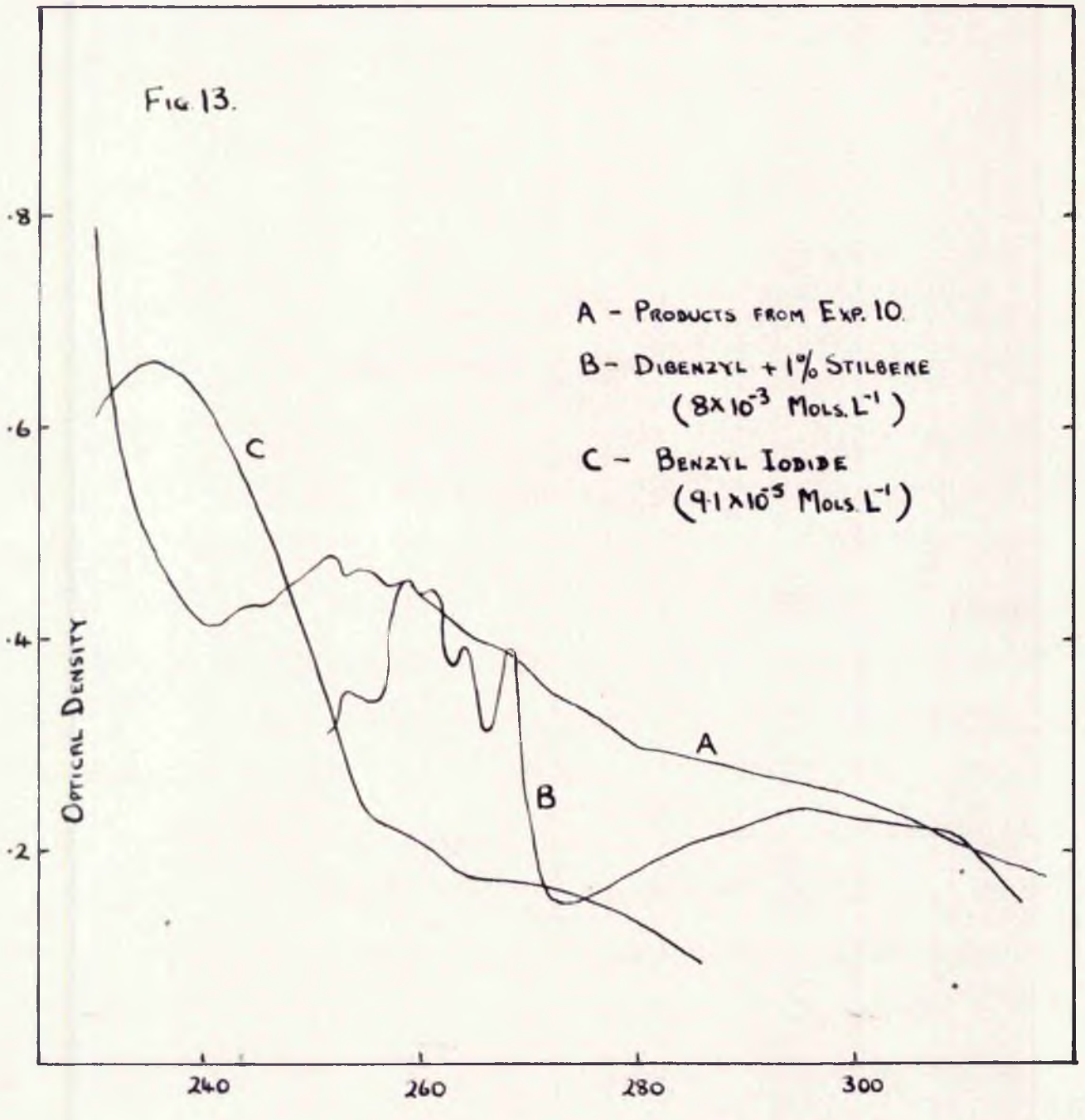


Fig 13 Ultra-Violet Spectra

Table 3

Exp. No.	Temp. °K	p.p. BzI in mm.	Moles I_2 formed/sec.	Moles Bz - Bz formed/sec.
10	650.5	.09	2.11×10^{-8}	2.07×10^{-8}
8	650	.068	2.23×10^{-8}	2.05×10^{-8}
4	650	.074	2.62×10^{-8}	2.50×10^{-8}

benzyl radicals, an obvious possibility being stilbene. A standard mass spectrum of stilbene was therefore obtained using the same conditions as for the dibenzyl calibrations. Comparison of this cracking pattern with that obtained from the solids in experiments Nos. 4, 8, 10, produced no evidence for the presence of stilbene. It must, however, be noted that the presence of up to 5% of stilbene in the dibenzyl could have remained undetected.

In addition to the mass spectrometer analyses, an ultra-violet spectroscopic examination was made of the solid products from experiment No. 10. Figure 13 shows the spectrum of a methanol solution of these products as well as the spectra of pure benzyl iodide and of dibenzyl, which contained 1% of stilbene. It is obvious from a comparison of these curves that the effect of even small amounts of benzyl iodide is to raise the general level of absorption in the dibenzyl region. Consequently, it seems very unlikely that the products in experiment 10 could have contained as much as 1% of stilbene, although the presence of small amounts of benzyl iodide and possibly free iodine, makes the data difficult to interpret.

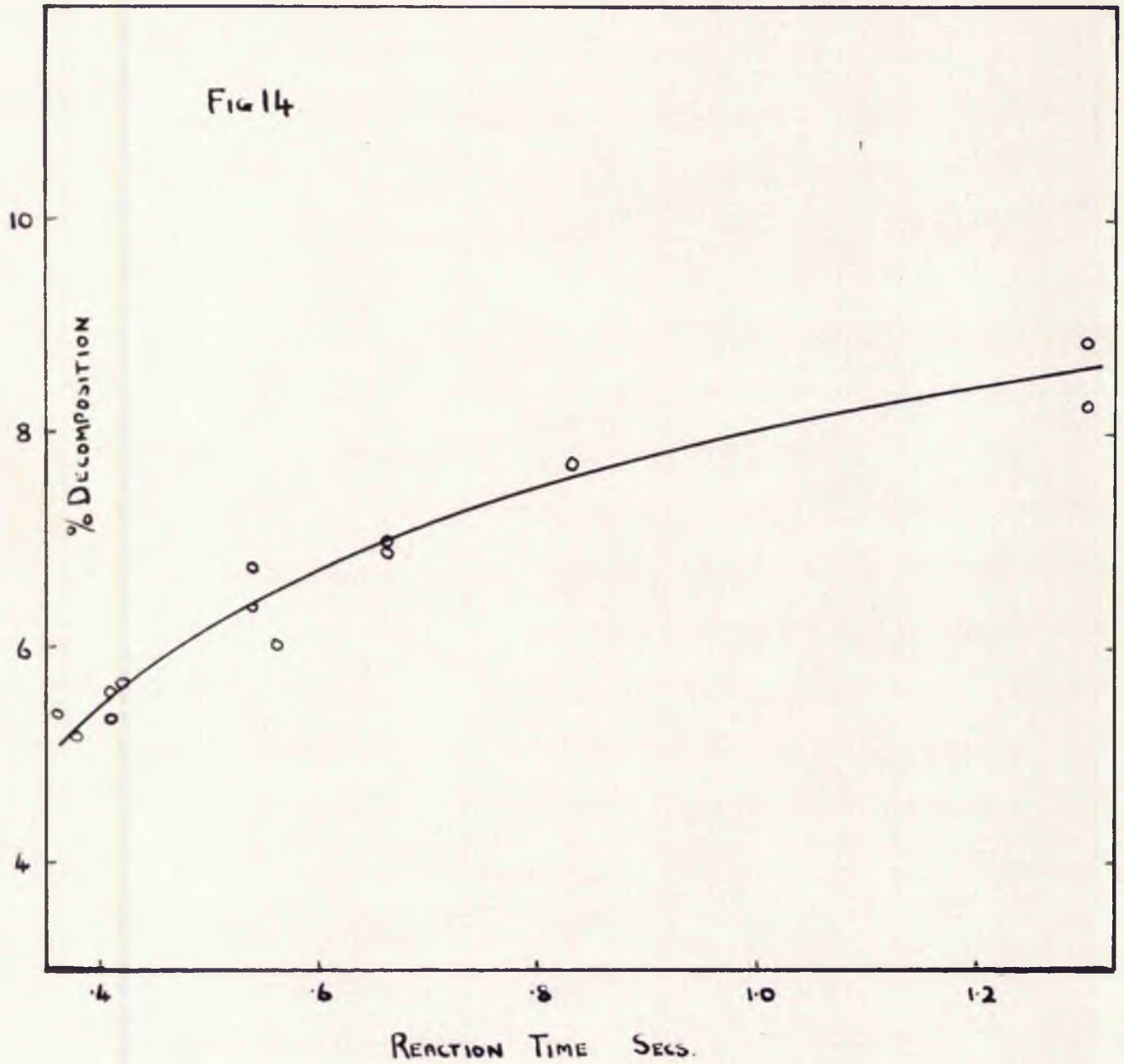


Fig 14. % Decomposition .v. Time of Reaction

The failure of mass spectrometry and ultra-violet spectroscopy to give any indication of significant amounts of a product other than dibenzyl, makes it seem reasonable to assume that we may represent the overall decomposition reaction by $2\ BzI \longrightarrow Bz-Bz + I_2$. All further calculations and deductions in this thesis have been carried out on this assumption.

Variation of Reaction Rate with Time of Reaction

If the decomposition of benzyl iodide is accompanied by some form of back reaction, then it is clear that the rate of reaction should decrease with increasing time of reaction. A short series of experiments was undertaken to prove this point and the results are shown in Table 4 and also in Figure 14. The experiments were conducted, as nearly as possible, with the same partial pressure of reactant and, of course, at the same temperature. The percentage decompositions shown in Table 4 have been calculated from the expression

$$\% \text{ decomposition} = \frac{\text{Conc. of iodine atoms}}{\text{Conc. of benzyl iodide injected}}$$

Figure 14 shows clearly that there is probably a rapid initial reaction which is being slowed down as the reaction time increases. This is exactly the behaviour to be expected if a back reaction were operative.

Table 4

Temperature 650-651 °K

Exp. No.	p.p. BzI in mm.	Reaction Time Secs.	% Decomposition
17	.075	.36	5.36
22	.070	.38	5.15
3	.074	.41	5.35
4	.074	.41	5.58
13	.077	.42	5.70
7	.068	.54	6.45
8	.068	.54	6.82
25	.071	.56	6.02
39	.071	.66	6.90
40	.071	.66	6.97
49	.070	.83	7.75
41	.081	1.20	8.20
42	.081	1.20	8.90

Derivation of a Possible Mechanism for the Decomposition

In view of the fact that dibenzyl and iodine appear to be the only products of the decomposition, the simplest mechanism which could account for the results is probably of the form shown below.

$$BzI \underset{}{\overset{Ke}{\longleftrightarrow}} Bz + I \longleftrightarrow \tfrac{1}{2} I_2$$
$$\Big\downarrow k_2 \qquad (1)$$
$$\tfrac{1}{2}\, Bz - Bz$$

It should be noted that the mechanism outlined does not imply any particular mode of back reaction.

The main obstacle in utilising this equation lies in deciding whether or not the two equilibria suggested are actually attained in our experimental conditions. If we assume that both the equilibria are established and that diffusion mixing in the reaction vessel is negligible, then we may derive the following rate expressions.

Let a = initial concentration of benzyl iodide

x = concentration of benzyl radicals

and α = fraction of iodine as atoms

Now, $$\frac{d(Bz - Bz)}{dt} = k_2(Bz)^2$$

But $$K_e = \frac{(Bz)(I)}{(BzI)}$$

therefore $$\frac{d(Bz - Bz)}{dt} = \frac{k_2 K_e^{\,2}(BzI)^2}{(I)^2}$$

or $$\frac{d(\frac{x}{2})}{dt} = \frac{k_2 K_2^{\,2}(a - x)^2}{\alpha^2 x^2}$$

therefore by integration,

$$\int_0^x \frac{\alpha^2 x^2}{(a - x)^2}\, dx = 2k_2 K_e^{\,2} t \qquad (2)$$

This last equation is capable of experimental proof since a graph of the integral on the left hand side of equation (2) against t (the time of reaction) should be a straight line whose slope is equal to $2k_2 K_e^{\,2}$. The simplest method of evaluating this integral is graphically

and this can only be done if data on the value of α are available. Fortunately, Perlman and Rollefson[78] have made some accurate measurements of the iodine dissociation equilibrium at several temperatures, and by extrapolation of their data it may be calculated that log. K_p at 650°K is -6.92. Although their data have been used throughout the present work, it is interesting to note that the value of -6.92, predicted from Perlman and Rollefson's data, agrees reasonably well with that obtained from much earlier results by Bodenstein[79]. Bodenstein's equation,

$$\log. K_p = \frac{-7550}{T} + 1.75 \log. T - .00409\,T + 4.726 \times 10^{-8} T^2 + .102$$

gives -6.83.

With this information, the value of α can be calculated for any given total concentration of iodine, by the following process.

Let P_I = partial pressure of total iodine expressed as atoms

i.e. $P_I = p_I + 2p_{I_2}$

where p_I = actual pressure of iodine as atoms.

p_{I_2} = actual pressure of iodine as molecules.

therefore

$$p_I = \alpha P_I \text{ and } p_{I_2} = \frac{(1-\alpha)P_I}{2}$$

$$\therefore \quad K_p = \frac{\alpha^2 P_I^2}{\frac{(1-\alpha)P_I}{2}}$$

$$\text{or } \log. K_p = \log. \frac{\alpha^2}{1-\alpha} + \log. P_I + \log. 2 \qquad (3)$$

In any particular experiment, the value of P_I is given by the percentage decomposition and therefore, α itself can readily be calculated from equation (3).

Since it is possible to obtain a value for α, it is clear that a graphical evaluation of the integral in equation (2) can be carried out. Perhaps the clearest way of showing how this may be done is by an actual example.

Example of the Evaluation of $\int \frac{\alpha^2 x^2}{(a-x)^2}\,dx$.

In experiment No. 3, we have

Partial pressure of benzyl iodide = .075 mm.

Temperature = 650°K.

Percentage decomposition = 5.35.

Thus

$$a = (BzI) = \frac{.075 \times 273}{22.4 \times 760 \times 650}$$

$$= 1.85 \times 10^{-6} \text{ mols./litre}$$

$$x = (\text{Total Iodine}) = \frac{5.35}{100} \times 1.85 \times 10^{-6}$$

$$= 9.9 \times 10^{-8} \text{ gatoms/litre}$$

$$\therefore P_I(\text{atms.}) = \frac{9.9 \times 10^{-8} \times 22.4 \times 650}{273}$$

$$= 5.27 \times 10^{-6} \text{ atms.}$$

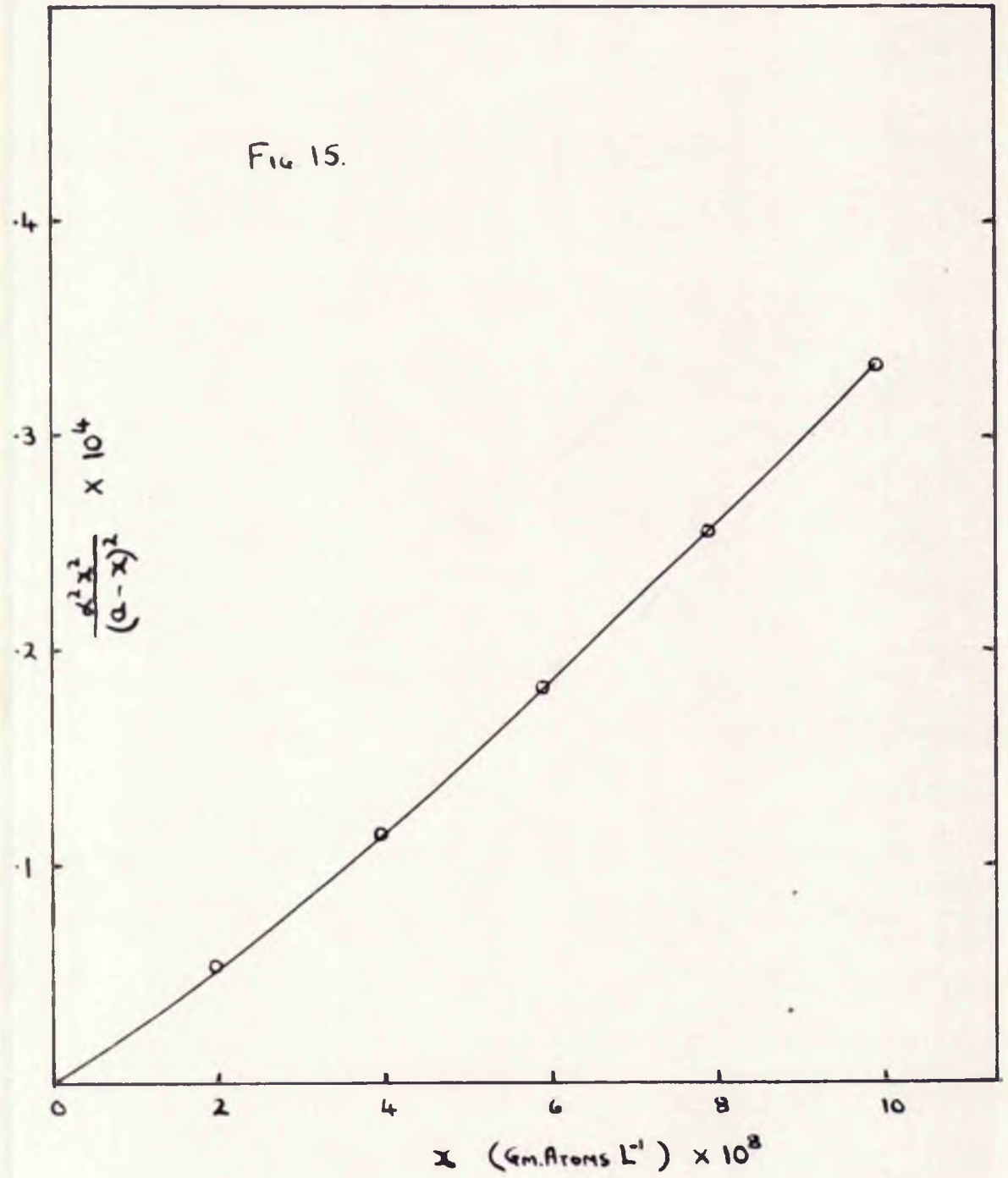


Fig. 15. $\frac{\alpha^2 x^2}{(a-x)^2}$ v. x for Exp. No. 3.

From Perlman and Rollefson's data, log. K_p at 650°K = -6.92 and therefore from equation (3), we get

$$\log. \frac{\alpha^2}{1-\alpha} = -6.92 - \log. 5.27 \times 10^{-6} - .301$$

$$= -1.945$$

hence $= 0.102$ (α is obtained directly from a graph of $\log. \frac{\alpha^2}{1-\alpha}$ v. α)

and $$\frac{\alpha^2 x^2}{(a-x)^2} = \frac{.102^2 \times 9.9^2 \times 10^{-16}}{175.1^2 \times 10^{-16}}$$

$$= 0.33 \times 10^{-4}$$

To integrate this function graphically, the value of $\frac{\alpha^2 x^2}{(a-x)^2}$, for various values of x, must be determined and a graph plotted of one against the other.

We have already shown that when P_I equals 5.27×10^{-6} atms. $\frac{\alpha^2 x^2}{(a-x)^2}$ equals $.33 \times 10^{-4}$ and we may similarly calculate the value of this function when the partial pressure of iodine (as atoms) equals $.8P_I$, $.6P_I$ etc. Figure 15 shows the results of this calculation. The value of the integral of $\frac{\alpha^2 x^2}{(a-x)^2}$ is given by the area, under the graph in Figure 15, as 1.51×10^{-12}.

The above example has dealt with the simplest case which involves the decomposition of benzyl iodide alone. However, the suggested mechanism of decomposition implies that the addition of iodine to the system will result in the extent of decomposition being decreased.

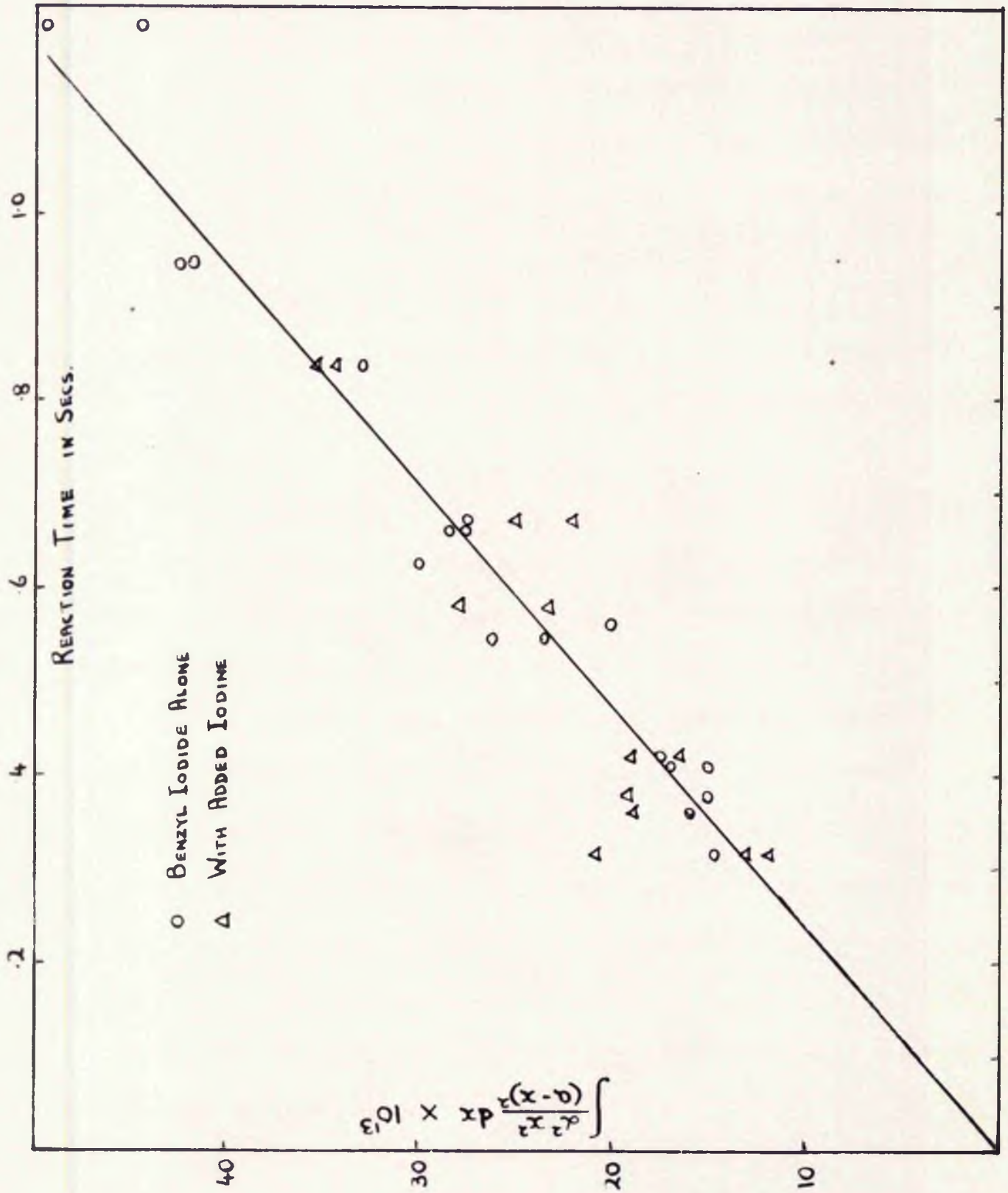


Fig. 16. $\int \frac{\alpha^2 x^2}{(a-x)^2} dx$. V. Reaction Time at 650·5°K

This is a direct consequence of the postulated equilibrium between benzyl iodide on the one hand and benzyl radicals and iodine atoms on the other. If the total concentration of added iodine, expressed as atoms, be c atoms per litre, then we can extend equation (2) to include this case by replacing x by (c + x).

i.e. $$\int \frac{\alpha^2(c + x)^2}{(a - x)^2}\, dx = 2k_2K_e^2t \qquad (4)$$

The integral in equation (4) can be evaluated in an analogous fashion to the described above.

Experimental Values of $\int \frac{\alpha^2(c + x)^2}{(a - x)^2}\, dx$ at various 'contact' Times

To test the validity of the type of mechanism, suggested in equation (1), a series of experiments was carried out, all at as near the same temperature as possible but with varying times of reaction. Some of the experiments were performed with, and some without, the presence of added iodine and the corresponding values of $\int \frac{\alpha^2(c + x)^2}{(a - x)^2}\, dx$ were calculated using the graphical method outlined in the previous section. The results are given in Table 5.

According to equation (4), a plot of $\int \frac{\alpha^2(c + x)^2}{(a - x)^2}\, dx$ against the contact time should be a straight line, the slope of which is equal to $2k_2K_e^2$. Such a plot is shown in Figure 16 from which a value of 4.25×10^{-12} for $2k_2K_e^2$ at 650.5°K (the mean temperature for this series of experiments) may be deduced.

Table 5

Temperatures 650-651 °K

Exp. No.	Reaction Time secs.	p.p. BzI mm.	p.p. Added Iodine mm. x 10^2	$\int \frac{\alpha^2(c+x)^2}{(a-x)^2} dx$ x 10^{12}
3	.41	.074	-	1.51
4	.41	.074	-	1.71
7	.54	.068	-	2.34
8	.54	.068	-	2.63
9	.95	.09	-	4.27
10	.95	.09	-	4.20
13	.42	.077	-	1.75
14	.42	.077	.21	1.68
15	.42	.077	.21	1.90
17	.36	.075	-	1.60
18	.36	.075	.11	1.75
19	.31	.063	-	1.46
20	.31	.063	.27	1.30
21	.31	.063	.27	1.20
22	.38	.070	-	1.50
23	.38	.070	.23	1.95
25	.56	.071	-	2.00
28	.62	.081	-	3.02
39	.66	.071	-	2.78
40	.66	.071	-	2.82
41	1.20	.081	-	4.30
42	1.20	.081	-	4.80
44	.58	.076	.167	2.33
45	.58	.076	.167	2.86
46	.67	.067	-	2.78
47	.67	.067	.199	2.20
48	.67	.067	.199	2.50
49	.83	.070	-	3.30
50	.83	.070	.244	3.53
51	.83	.070	.244	3.46

Two further similar series of experiments were carried out at 663°K and 674°K and the results are given in Tables 6 and 7 respectively.

Table 6

Temperatures 662-662 °K

Exp. No.	Reaction Time secs.	p.p. BzI mm.	p.p. Added Iodine mm. x 10^2	$\int \frac{\alpha^2(c+x)^2}{(a-x)^2} dx$ x 10^{12}	$2k_2K_e^2$ x 10^{11}
87	.53	.096	-	6.54	1.23
88	.53	.096	-	6.84	1.28
89	.53	.096	.17	7.08	1.33
90	.60	.112	-	6.54	1.09
91	.60	.112	-	6.23	1.04
92	.60	.112	.20	6.20	1.0
93	.36	.041	-	2.80	0.78
94	.36	.041	-	2.79	0.77
95	.36	.041	.141	5.30	1.46
96	.83	.032	-	7.10	0.86
97	.83	.032	-	7.10	0.86
98	.83	.032	.586	9.48	1.14
99	.55	.030	-	5.2	0.95
100	.55	.030	-	5.2	0.95
101	.79	.034	-	6.82	0.86
102	.79	.034	-	8.0	1.07
103	.79	.034	.104	9.4	1.18
104	.81	.20	-	8.4	1.04
105	.81	.20	-	8.4	1.04
107	.51	.148	-	6.5	1.28
108	.51	.148	-	6.8	1.33
109	.51	.148	.108	9.4	1.80
110	.37	.046	-	4.6	1.24
111	.37	.046	-	3.9	1.05
112	.37	.046	.061	3.5	0.95

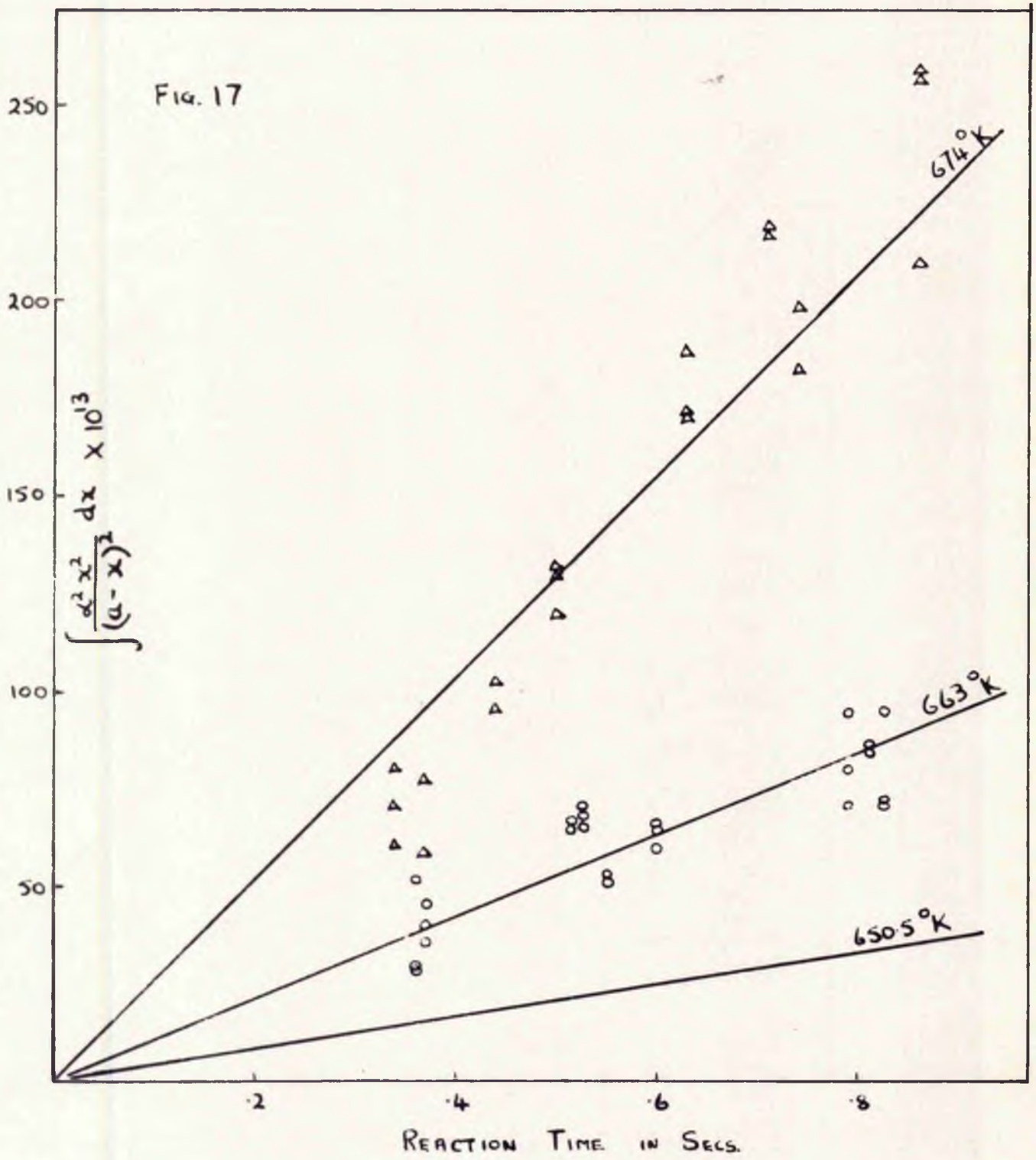


FIG. 17. $\int \frac{\alpha^2 x^2}{(a-x)^2} dx$ V. REACTION TIME AT 663° AND 674°K.

Table 7

Temperatures 673-674 °K

Exp. No.	Reaction Time secs.	p.p. BzI mm.	p.p. Added Iodine mm. x 10^2	$\int \frac{\alpha^2(c+x)^2}{(a-x)^2} dx$ x 10^{12}
52	.34	.071	-	8.0
53	.34	.071	-	7.1
54	.34	.071	.154	6.1
55	.37	.069	-	7.8
57	.37	.069	.206	5.8
61	.70	.094	-	21.7
62	.70	.094	-	22.2
64	.44	.065	-	9.6
65	.44	.065	-	10.2
67	.63	.08	-	17.2
68	.63	.08	-	18.7
69	.63	.08	.238	17.1
70	.74	.093	-	18.1
72	.74	.093	.425	19.8
73	.50	.078	-	12.8
74	.50	.078	-	13.1
75	.50	.078	.26	12.2
76	.86	.091	-	26.1
77	.86	.091	-	26.1
78	.86	.091	.175	21.0

These results are also shown in Figure 17 - the results obtained at 650.5°K being included for comparison. From the gradient of the lines in Figure 17, the values of $2k_2K_e^2$ (see equation (4)) may be calculated as 2.6×10^{-11} at 674°K and 1.06×10^{-11} at 663°K.

It is, of course, possible to calculate a value for $2k_2K_e^2$ from any

one experiment by merely dividing the value of the integral of $\frac{\alpha^2 x^2}{(a-x)^2}\,dx$ by the contact time. This calculation has been carried out for the experiments at 663°K and the results are given in the final column of Table 6. Neglecting the result of experiment No. 109, the average value of $2k_2K_e^2$ is 1.07×10^{-11}, the standard deviation being 0.18×10^{-11}. Although each individual result is obviously much less accurate than the value obtained from Figure 17, they can be used to demonstrate that, within experimental limits, the value of $2k_2K_e^2$ is independent of the concentration of benzyl iodide, e.g. at 0.03 mm. benzyl iodide, the average value is 0.95×10^{-11} whereas at 0.20 mm. it is 1.04×10^{-11}. Thus a sevenfold increase in the partial pressure of benzyl iodide has not significantly affected the value of $2k_2K_e^2$.

The experimental results, recorded in Tables 5, 6 and 7, are consistent with the mechanism outlined in equation (1), i.e. they are in accord with the theory that the recombination rate of two benzyl radicals is an irreversible process which results in the withdrawal of benzyl radicals from an equilibrium system involving benzyl iodide, iodine atoms and iodine molecules. The results are also in agreement with the suggestion that both of the postulated equilibria are, in fact, established in the reaction zone.

Variation of $2k_2K_e^2$ with Temperature

In the preceding section, values of $2k_2K_e^2$ at 650.5°K, 663°K and 674°K, were obtained from the results of a large number of experiments

at each temperature. Duplicate experiments, at four other temperatures, were also conducted and the results are given in Table 8.

Table 8

Exp. No.	Temp. °K	Reaction Time in secs.	p.p. BzI mm.	$\int \frac{\alpha^2 x^2}{(a-x)^2} dx \times 10^{12}$	$2k_2K_e^2 \times 10^{12}$
79	702	.30	.072	139.8	465
80	702	.30	.072	151.8	505
81	685	.37	.075	29.6	80.0
82	685	.37	.075	20.8	57.0
83	611	.86	.085	.0183	.0212
84	611	.86	.085	.0175	.0205
85	632	.86	.086	.402	.468
86	632	.86	.086	.391	.455

Data are thus available on the variation of $2k_2K_e^2$ over a temperature range of about 100°C. This function is the product of a rate constant and the square of an equilibrium constant and it is apparent that a value for the temperature independent factor can be calculated. However, the accuracy of the value obtained can obviously be increased if the temperature range is extended. Although the reaction is too slow, at temperatures below 610°K, to be conveniently studied by the flow technique, the use of a static system with much longer reaction times, would enable the reaction to be studied at temperatures appreciably below 600°K. Experiments, carried out using such a system, are described in the following section.

1.2 EXPERIMENTS USING A STATIC SYSTEM

A detailed description of the method by which these static system experiments were performed has already been given in the section entitled 'Apparatus and Experimental Technique'.

It was observed that, when the products were being pumped out of the reaction vessel, traces of a white solid were usually left on the vessel walls. A micro-determination of the melting-point of this solid gave it as 45°C and it is, therefore, likely that the solid was dibenzyl (m. pt. 52°C) which would be expected to distil only rather slowly out of the reaction vessel. The ultra-violet spectrum of a methanol solution of the solid confirmed the suggestion that it was dibenzyl.

A major difference between the static and flow systems is that much higher concentrations of reactant must be used in the former to obtain enough product for an accurate analysis to be performed. Thus, in this series of experiments the concentration of benzyl iodide was usually of the order of 10^{-4} mols./l. whereas in the flow experiments it was generally of the order of 10^{-6} mols./l. Therefore, the experiments using the static system not only make it possible to study the reaction at lower temperatures but also provide the opportunity of testing the postulated rate equations at much higher benzyl iodide concentrations.

Altogether eight successful experiments were carried out at temperatures ranging from 516 to 557°K. The results are shown in Table 9 - the calculations having been carried out in an analogous manner to those for the flow system results recorded previously.

Table 9

Exp. No.	Temp. °K	Reaction Time in secs. x 10^{-3}	Benzyl Iodide conc. in mols./l. x 10^{4}	$\int \frac{\alpha^2 x^2}{(a-x)^2} dx$ x 10^{14}	$2k_2K_e^2$ x 10^{19}
S1	557	3.6	1.75	27.4	764
S3	534	10.26	1.66	2.56	25.0
S4	534	11.4	2.2	1.74	15.2
S5	545	7.02	0.67	5.88	84.0
S6	545	7.62	2.69	6.82	89.2
S7	553	6.0	1.09	29.7	479
S8	516	20.5	2.60	.534	2.48
S9	519	15.3	2.76	.387	2.53

Experiments S5 and S6 show clearly that the function $2k_2K_e^2$ is independent of the benzyl iodide concentration.

1.3 THE TEMPERATURE DEPENDENCE OF THE FUNCTION $2k_2K_e^2$

Combining the results obtained by the flow and static methods, data are available on the values of $2k_2K_e^2$ over the large range of temperatures of 186°C - from 516°K to 702°K.

K_e has been defined as the equilibrium constant for the reaction BzI $\longrightarrow$ Bz + I and therefore according to the Van't Hoff isochore we may write

$$\frac{d(\ln K_e)}{dT} = \frac{\Delta H}{RT^2}$$

(where ΔH equals the enthalpy change of the reaction)

$$\text{or} \quad \ln K_e = \frac{\Delta H}{RT} + \text{const.} \qquad (5)$$

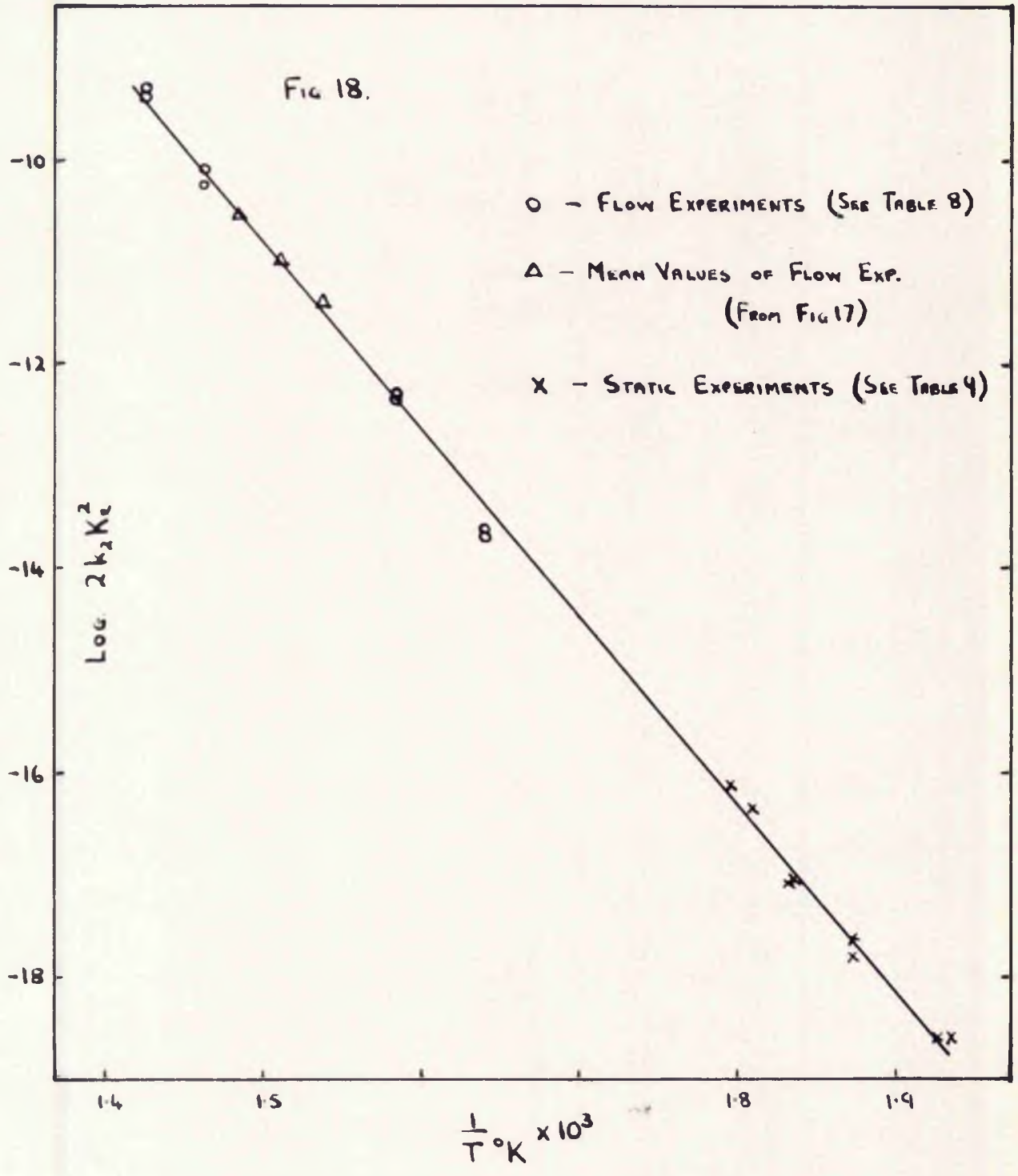


Fig 18. Logarithm of $2k_2K_c^2$ v. $\frac{1}{T°K}$

Similarly k_2 has been defined as the rate constant for the recombination of two benzyl radicals and we may write

$$k_2 = Be^{-\frac{E}{RT}}$$

$$\text{or} \quad \ln.k_2 = \ln B - \frac{E}{RT} \qquad (6)$$

Combining equations (5) and (6) it is obvious that

$$\ln.k_2K_e^2 = -\left(\frac{2\,\Delta H}{RT} + \frac{E}{RT}\right) + \text{const.}' \qquad (7)$$

Thus, if from collected data on $2k_2K_e^2$, a graph of log. $2k_2K_e^2$ against the reciprocal of the absolute temperature is plotted, then the slope of the straight line obtained will be equal to $\frac{2\,\Delta H + E}{2.3\,R}$. Such a plot is shown in Figure 18 which leads to a value of 84 K cal./mol. for $(2\,\Delta H + E)$. Since E is the energy required for the recombination of two similar free radicals its value is likely to be small and may even by zero. The highest reported activation energy for the recombination of two similar free radicals is that for triphenyl methyl radicals, which is given by Ziegler[80] as 7 K cal./mol.; it would, therefore, seem reasonable to assume that the much less hindered benzyl free radicals would require less energy than this to dimerize.

If it is assumed that for two benzyl radicals the recombination energy is in fact zero, then, from the results in Figure 18, ΔH for the benzyl iodide equilibrium may be calculated as 42 K cal./mol. This is the maximum value of the carbon-iodine bond strength and this value

must be reduced by 1 K cal./mol. for every 2 K cals. of activation energy required by the recombination of two benzyl radicals. Since it is likely that this latter energy is not more than 4-5 K cal./mol., it is concluded that, on the basis of the experiments summarised in Figure 18, the carbon iodine bond strength in benzyl iodide must lie between 40 and 42 K cal./mol.

2. THE DECOMPOSITION OF BENZYL IODIDE IN THE PRESENCE OF A RADICAL ACCEPTOR

2.1 INTRODUCTION

It has been demonstrated that, in the decomposition of benzyl iodide, a reverse reaction takes place which is increased in rate by the presence of iodine. In order to study a reaction without the interference of a complicating reverse reaction, it has been common practice to use a radical acceptor e.g. the toluene carrier technique used to a great extent by Szwarc[81]. The underlying principle of this method is to introduce to the system a compound, such as toluene, which contains a relatively weak bond and which is therefore an energetically favoured target for free radical attack. For example, toluene can be used to trap methyl radicals with which it reacts to produce methane and relatively inactive benzyl radicals. Since methane has a much stronger carbon hydrogen bond than toluene, this reaction obviously represents an energy gain by the system. Unfortunately toluene cannot be used in a study of the decomposition of benzyl iodide because neither the benzyl radical nor the iodine atom, formed by the decomposition of the iodide, would react with toluene since both dibenzyl and benzyl iodide (the possible products) contain weaker bonds than the carbon hydrogen bond of toluene itself. However, hydrogen iodide, with a bond strength of 71 K cal./mol. offers a convenient radical acceptor for the benzyl iodide system. In theory, the reactions to be expected, when benzyl iodide is decomposed in the presence of hydrogen iodide, are:-

$$BzI \longrightarrow Bz + I \qquad (1)$$

$$Bz + HI \longrightarrow Bz{\cdot}H + I \qquad (2)$$

$$M + I + I \longrightarrow I_2 + M \qquad (3)$$

When the hydrogen iodide is present in considerable excess over the benzyl iodide, then, assuming reaction (2) to have a low or zero energy of activation, it might be expected that this reaction would remove the benzyl radicals from the system too quickly to permit their reaction with iodine atoms or molecules to reform benzyl iodide. Thus the decomposition should become a unimolecular process. This part of the thesis describes experiments which were carried out using a system as suggested above.

2.2 IDENTIFICATION OF PRODUCTS

Apart from iodine, the only product to be expected in the decomposition of benzyl iodide in the presence of excess hydrogen iodine is toluene. Although no attempt was made to estimate toluene quantitatively, it was identified, by means of its ultra-violet spectrum, in the reaction products.

2.3 EFFECT OF PARTIAL PRESSURE OF HYDROGEN IODIDE ON THE PERCENTAGE DECOMPOSITION

If hydrogen iodide acts as a radical acceptor, then, provided a certain excess of hydrogen iodide over benzyl iodide is maintained, the decomposition rate should be virtually independent of the actual amount of hydrogen iodide present. Further, if the mechanism outlined in 2.1 is correct, the percentage decomposition of benzyl iodide should

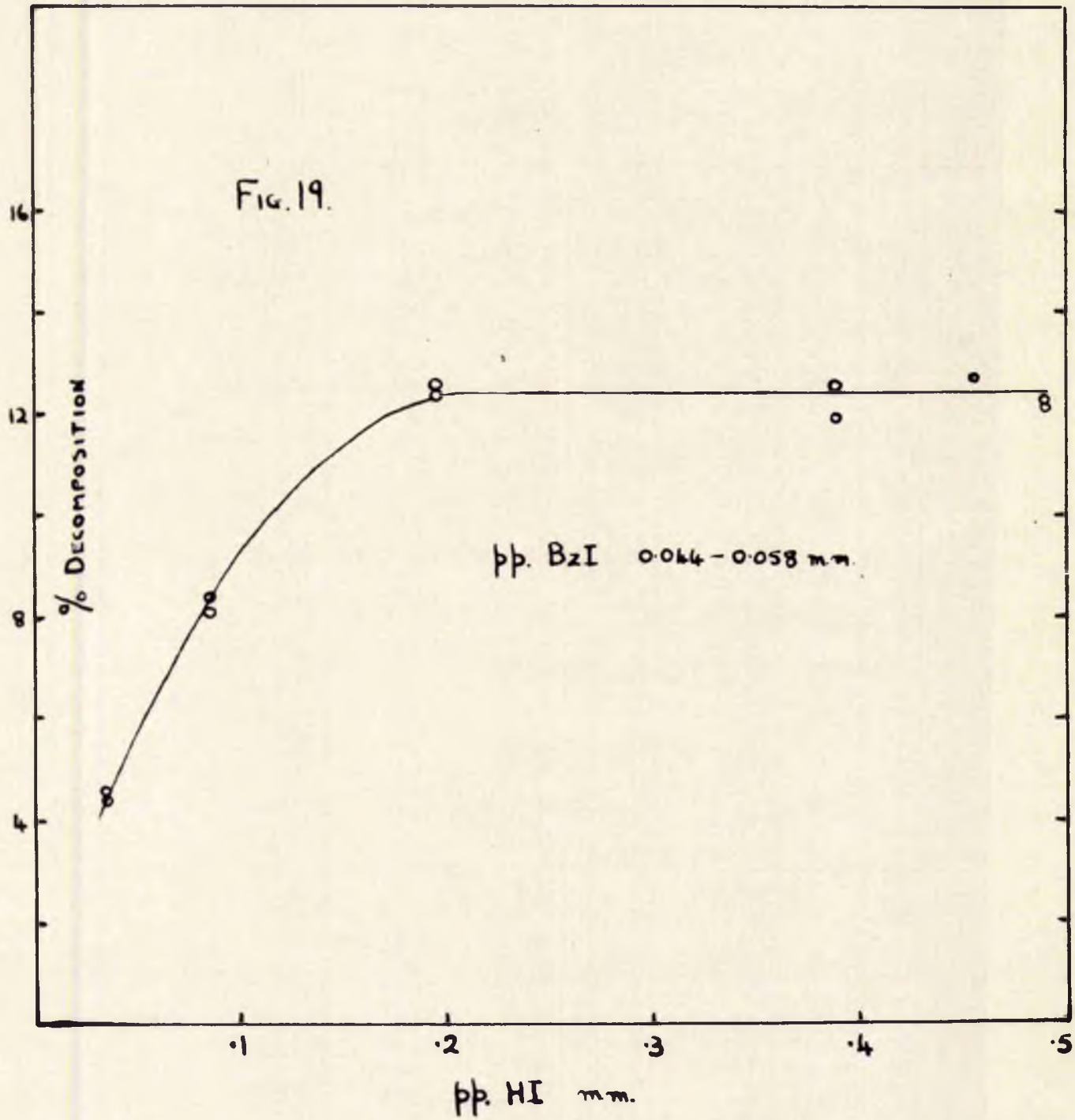


Fig. 19. Effect of HI on the Decomposition Rate

decrease with decreasing concentrations of hydrogen iodide when the concentration of the latter falls below the prescribed excess.

A few experiments, carried out at 585°K, demonstrate that the type of behaviour, suggested above, is found in practice. The experiments were performed with as near the same times of reaction as possible and with approximately constant partial pressures of benzyl iodide. It was not possible, however, to obtain exactly the same reaction time from one experiment to another due to the nature of the flow apparatus and consequently the percentage decompositions have been corrected to a time of 0.54 sec. (In order to make this correction, it has been assumed that, over the short range of times involved, the percentage decomposition is directly proportional to the time of reaction). The results of these experiments are given in Table 10.

Table 10

Temperature 585°K

Experiment No.	Reaction time in secs.	p.p. BzI mm.	p.p. HI mm.	% Decomp. corrected to 0.54 sec.
121	.54	.044	.488	12.2
122	.54	.044	.488	12.1
123	.54	.048	.388	11.9
124	.54	.048	.388	12.6
126	.58	.047	.20	12.6
127	.58	.047	.20	12.4
129	.58	.055	.084	8.1
130	.58	.055	.084	8.4
132	.55	.058	.035	4.5
133	.55	.058	.035	4.6

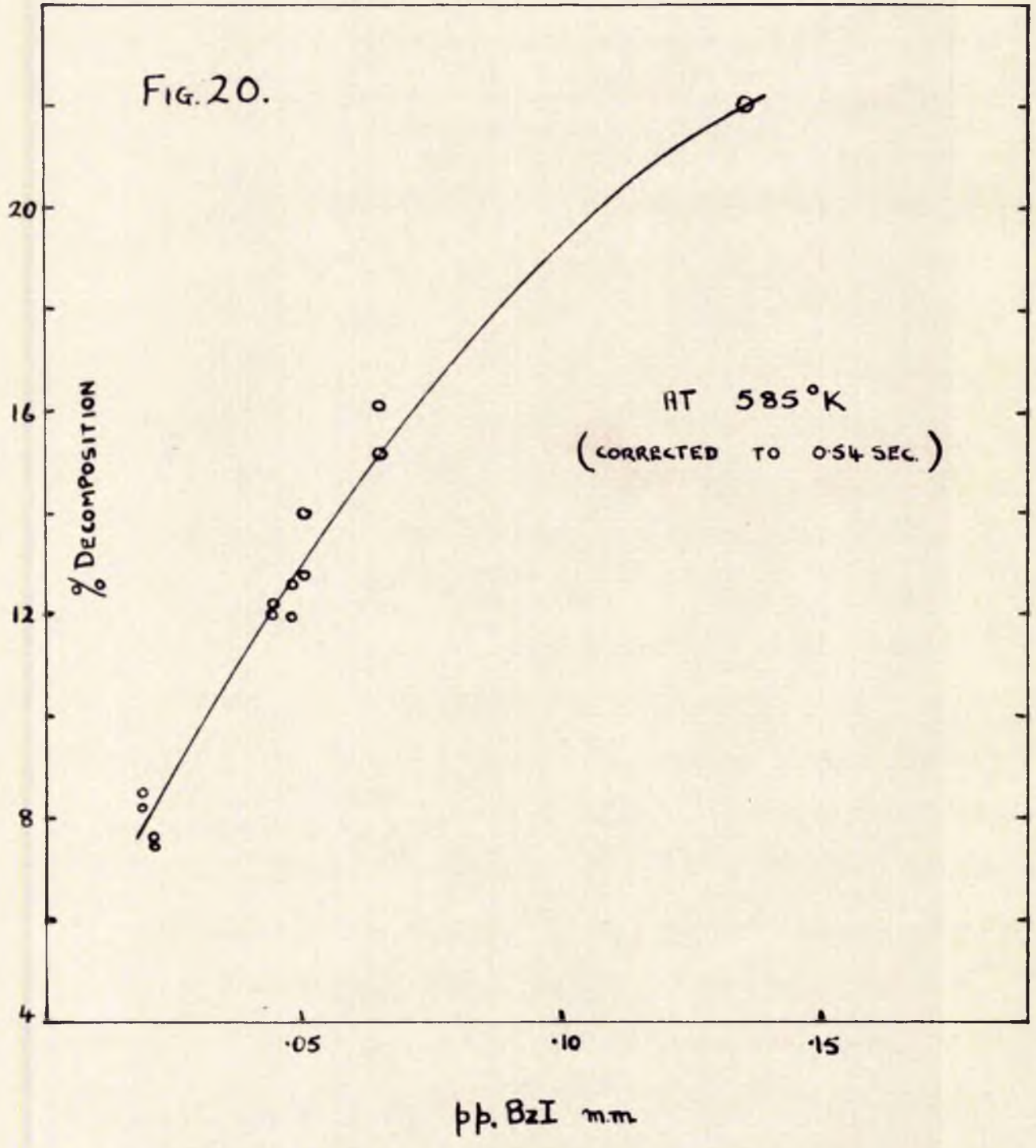


FIG. 20. EFFECT OF BzI CONCENTRATION ON % DECOMPOSITION

The results are also presented in Figure 19 from which it is clear that, once a certain excess of hydrogen iodide is achieved the rate of decomposition becomes virtually independent of the extent of the excess.

2.4 EFFECT OF VARYING THE BENZYL IODIDE CONCENTRATION

When a sufficient excess of hydrogen iodide is present, the rate determining step in the decomposition should be the initial dissociation of the benzyl iodide molecule. A series of experiments, at 585°K, was carried out to determine the effect of variations in the benzyl iodide concentration on the rate. At least a sixfold excess of hydrogen iodide over benzyl iodide was maintained throughout the series.

The results are given in Table 11 and are also shown in Figure 20 - on the graph the "corrected" percentage decompositions (corrected to a reaction time of 0.54 sec.) are plotted against the partial pressures of benzyl iodide.

It is immediately evident from Figure 20 that the rate of decomposition, under these conditions, is markedly dependent on the concentration of benzyl iodide. This implies that, even in the presence of sufficient hydrogen iodide to prevent the occurrence of a reverse reaction, the decomposition is not a first order reaction and is indeed approximately second order at the lowest pressures used.

Table 11

Temperature 585°K

Experiment No.	Reaction time in secs.	p.p. BzI mm.	p.p. HI mm.	% Decomp. corrected to 0.54 sec.
135	.54	.020	.266	7.6
136	.54	.020	.266	7.5
138	.57	.020	.254	8.6
139	.57	.020	.254	8.3
121	.54	.044	.488	12.2
122	.54	.044	.488	12.1
126	.58	.047	.200	12.6
127	.58	.047	.200	12.4
123	.54	.048	.388	11.9
124	.54	.048	.388	12.6
141	.52	.050	.455	12.8
142	.52	.050	.455	14.2
144	.51	.065	.585	15.2
145	.51	.065	.585	16.2
153	.50	.134	.885	22.0

The collision theory of unimolecular reactions predicts that all such reactions should tend towards second order as the pressure of reactant is decreased and it was thought that the intermediate order observed in the decomposition of benzyl iodide was due to this low pressure effect. (The development of the Hinshelwood-Lindemann mechanism for unimolecular reactions and some of its subsequent modifications are discussed in Appendix 2). Although there is relatively little direct experimental evidence available on the order transition in the case of molecules containing as many atoms as benzyl iodide, Slater[82] has predicted that at pressures of the order of 10^{-1} mm.

a thirteen atom molecule would be in its transition region. Since theory demands that the more complex the molecule the lower will be the pressure at which the rate ceases to be first order, benzyl iodide, with fifteen atoms, might be expected to exhibit transition effects at slightly less than 10^{-1} mm. Probably the most complex molecule which has been thoroughly investigated, at both high and low pressures, is cyclo-butane. The decomposition of this compound was shown by Genaux and Walters[83] and Kern and Walters[84] to be first order at pressures of over 100 mm. and to have fallen to about one third of its high pressure rate at 10^{-1} mm.

A possible method of checking whether the observed variation in the rate of decomposition of benzyl iodide with partial pressure of reactant is due to a first to second order transition would be to determine the effect of varying the inert gas pressure. If a genuine first to second order transition is being observed then the rate should increase with increasing inert gas pressure, since even "inert" gases may cause activation by collision.

2.5 EFFECT OF INERT GAS PRESSURE

In these experiments the benzyl iodide and hydrogen iodide partial pressures and the time of reaction were maintained as nearly constant as possible.

(a) Variation of Nitrogen Pressure

The effect on the reaction rate of varying the nitrogen pressure from 2.0 mm. to 9.9 mm. was investigated in a series of experiments at 574°K. The results are given in Table 12 and are

FIG. 21 (a)

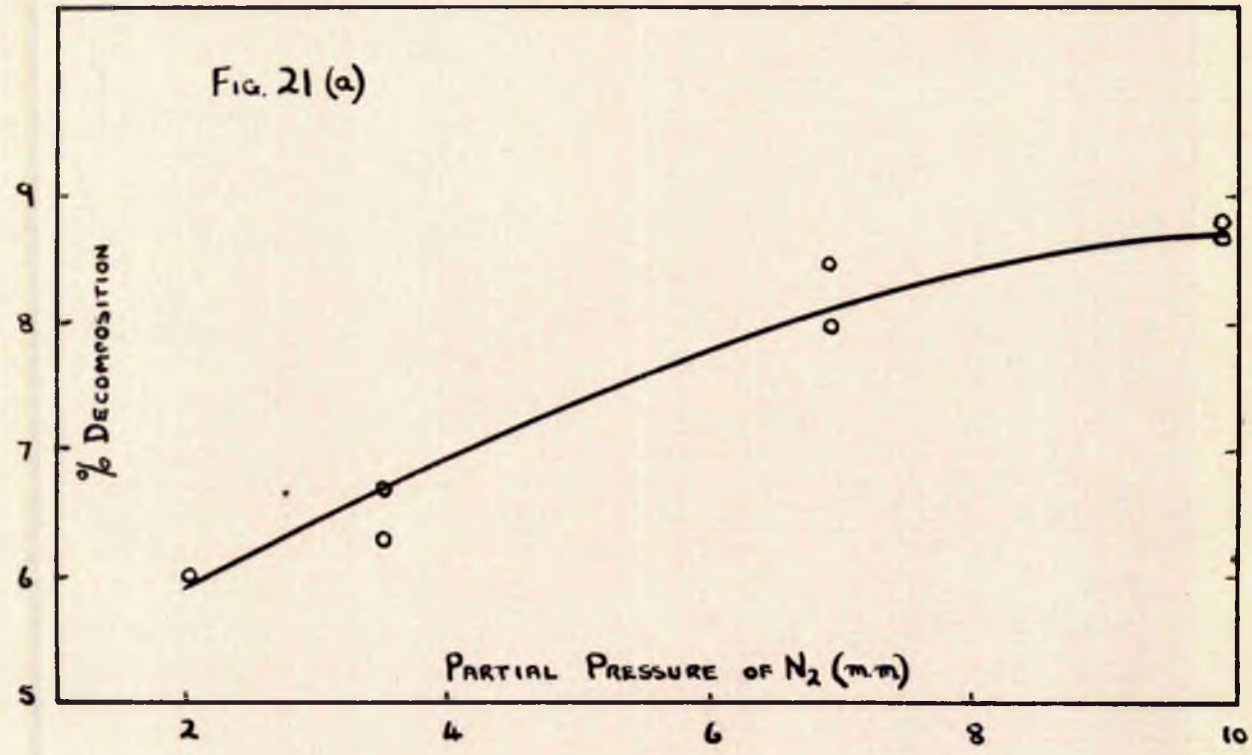
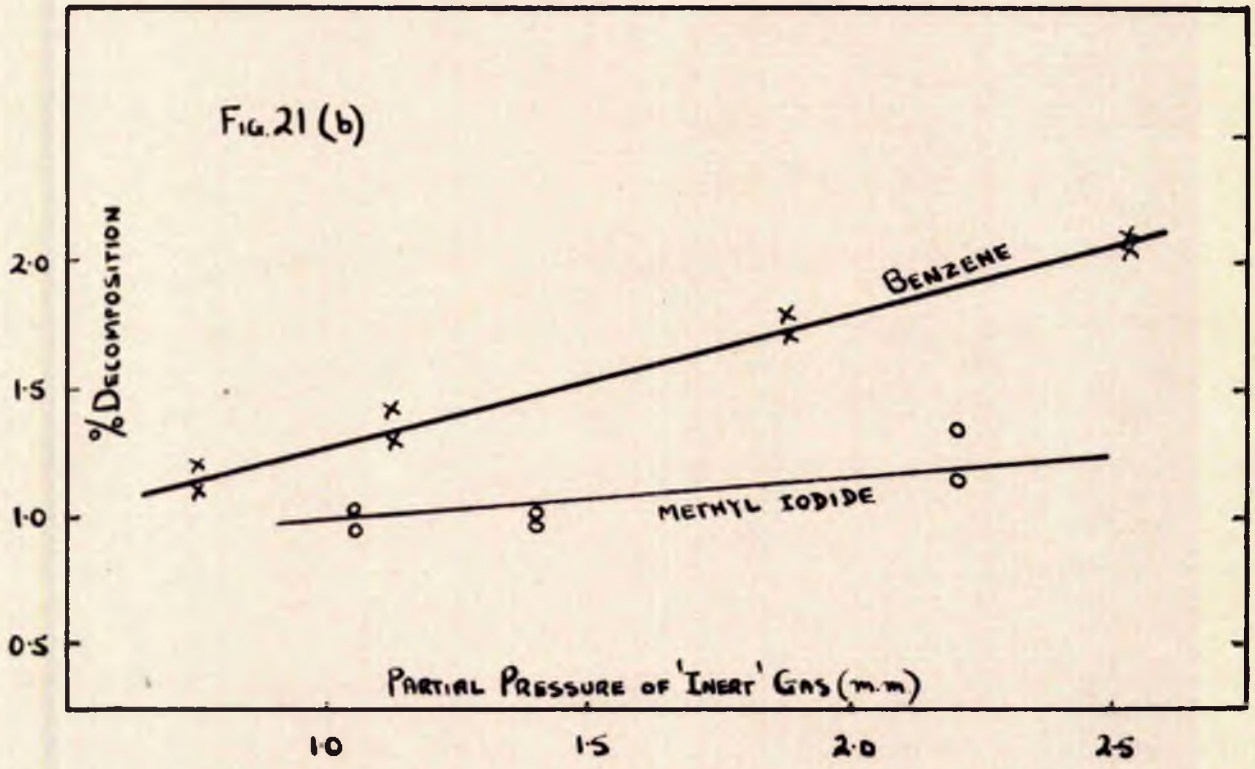


FIG. 21 (b)



illustrated in Figure 21a.

Table 12

Temperature 574°K

Experiment No.	Reaction Time secs.	p.p. BzI mm.	p.p. HI mm.	p.p. N_2 mm.	% Decomp. corrected to 0.41 sec.
156	.41	.047	.472	3.5	6.3
157	.41	.047	.472	3.5	6.7
158	.41	.050	.471	6.9	8.0
159	.41	.050	.471	6.9	8.5
162	.44	.050	.452	9.9	8.7
163	.44	.050	.452	9.9	8.8
164	.44	.048	.460	2.0	6.0

The effect of the partial pressure of nitrogen is seen to be small but is nevertheless significant.

(b) Variation of Hydrogen Iodide Pressure

In Section 2.3, it was shown that, at low hydrogen iodide to benzyl iodide ratios, the reaction rate was markedly dependent on hydrogen iodide concentration but that once enough hydrogen iodide was present to eliminate the recombination reaction, the rate became independent of the pressure of hydrogen iodide. Obviously if this system is in the transition region of a unimolecular reaction, the rate should still be slightly dependent on the hydrogen iodide concentration even in the presence of an excess, due to the activating effect of the hydrogen iodide molecules. A single experiment was carried out at a much higher partial pressure of hydrogen iodide than in the previous

work (Section 2.3) and this result, together with those from Table 10, has been included in Table 13 - all the results being corrected to 0.54 sec. reaction time and 0.048 mm. partial pressure of benzyl iodide.

Table 13

Temperature 585°K

N_2 Pressure 3.7 - 3.9 mm.

Experiment No.	Reaction Time secs.	p.p. BzI mm.	p.p. HI mm.	Corrected % Decomp.
121	.54	.044	.488	13.3
122	.54	.044	.488	13.1
123	.54	.048	.388	11.9
124	.54	.048	.388	12.6
126	.58	.047	.200	12.9
127	.58	.047	.200	12.7
148	.50	.053	2.20	15.7

It is evident from these results that, above the critical pressure of hydrogen iodide, there is only a very slight dependence of rate on the hydrogen iodide concentration. This slow increase in rate, at pressures above about 0.2 mm. of hydrogen iodide, could be due to the activating effect of the hydrogen iodide on the benzyl iodide molecules.

(c) Variation of Benzene Pressure

It is generally accepted that the efficiency of energy transfer by an inert gas increases with the complexity of the molecule at least until apparent maximum efficiency is reached when further complexity leads to no further increase in the transfer efficiency. Several experiments were therefore carried out in which varying partial

pressures of benzene were added to the system. Although benzene does not seem to have been used for this purpose before, it was selected, in preference to toluene, which has been shown to be very efficient at activating the decomposition of cyclopropane[85] and cyclobutane[86], because it was thought less likely to react with the hydrogen iodide present in the system. A trial experiment, under normal experimental conditions, showed that no interaction between hydrogen iodide and benzene took place.

The results of the experiments with added benzene are given in Table 14 and are also shown in Figure 21b. The percentage decompositions have, as usual, been corrected to a constant contact time viz. 0.44 secs. and they have also been corrected for slight variations in the benzyl iodide partial pressure. The latter correction has been made on the assumption that the reaction is second order and it has already been shown (Section 2.4) that this is approximately true at the low partial pressures involved. The results have been corrected to a benzyl iodide partial pressure of 0.013 mm.

Although the experiments on the nitrogen and benzene variations were unfortunately carried out under different experimental conditions, it is nevertheless apparent that benzene has a much greater effect on the reaction than has nitrogen.

Table 14

Temperature 558-559°K

N_2 Pressure 1.47-1.55 mm.

Experiment No.	Reaction Time secs.	p.p. BzI mm.	p.p. HI mm.	p.p. Ph·H mm.	Corrected % Decomp.
223	.44	.0114	.482	1.88	1.72
224	.44	.0114	.482	1.88	1.81
227	.42	.013	.471	0.75	1.10
228	.42	.013	.471	0.75	1.19
229	.42	.0133	.462	2.52	2.04
230	.42	.0133	.462	2.52	2.08
232	.45	.0149	.510	1.13	1.31
233	.45	.0149	.510	1.13	1.42

(d) Variation of Methyl Iodide Pressure

Since it is presumably the carbon-iodine bond in benzyl iodide which must acquire sufficient energy to cause decomposition, it was considered that the introduction of a non-reacting molecule containing a carbon-iodine bond might result in greatly increased reaction rates. For this reason, methyl iodide was selected as a possibly efficient inert gas. Preliminary experiments demonstrated that methyl iodide did not decompose under the experimental conditions and did not react with hydrogen iodide. Using similar conditions to those used in the benzene addition experiments, a few experiments at several different partial pressures of methyl iodide were carried out and the results are recorded in Table 15 and Figure 21b.

Table 15

Temperature 558° K

N_2 Pressure 1.53-1.57 mm.

Experiment No.	Reaction time secs.	p.p. BzI mm.	p.p. HI mm.	p.p. CH_3I mm.	Corrected* % Decomp.
238	.42	.0121	.452	1.40	0.96
239	.42	.0121	.452	1.40	1.00
241	.44	.0118	.45	.995	1.05
243	.44	.0118	.45	.995	0.96
246	.40	.012	.45	2.2	1.33
247	.40	.012	.45	2.2	1.13

* Corrected to 0.44 sec. reaction time and 0.012 mm. partial pressure of BzI.

It is immediately clear from Figure 21b that methyl iodide is much less effective than benzene in increasing the decomposition rate of the benzyl iodide. The graph also shows that both the methyl iodide and the benzene curves cut the vertical axis at approximately the same percentage decomposition. Since both series of experiments involve about 1.5 mm. of nitrogen and 0.45-0.5 mm. of hydrogen iodide in addition to the methyl iodide or benzene, this intercept is presumably the percentage decomposition in the presence of only the nitrogen and the hydrogen iodide.

(e) Variation of Surface Area to Volume Ratio

Previous workers at St. Andrews[5, 6, 7] have noted that in the first to second order transition region for methyl and trifluoromethyl iodides, a distinct wall effect was observed.

A limited number of experiments were carried out on the decomposition of benzyl iodide, in the presence of HI, in a Pyrex furnace; the furnace had removable sleeves so that the surface area to volume ratio could be readily altered.

The results of these experiments are difficult to interpret and since they do not affect the main thesis, they are included in an appendix (see Appendix 3).

2.6 RELATIVE EFFICIENCIES OF THE VARIOUS INERT GASES

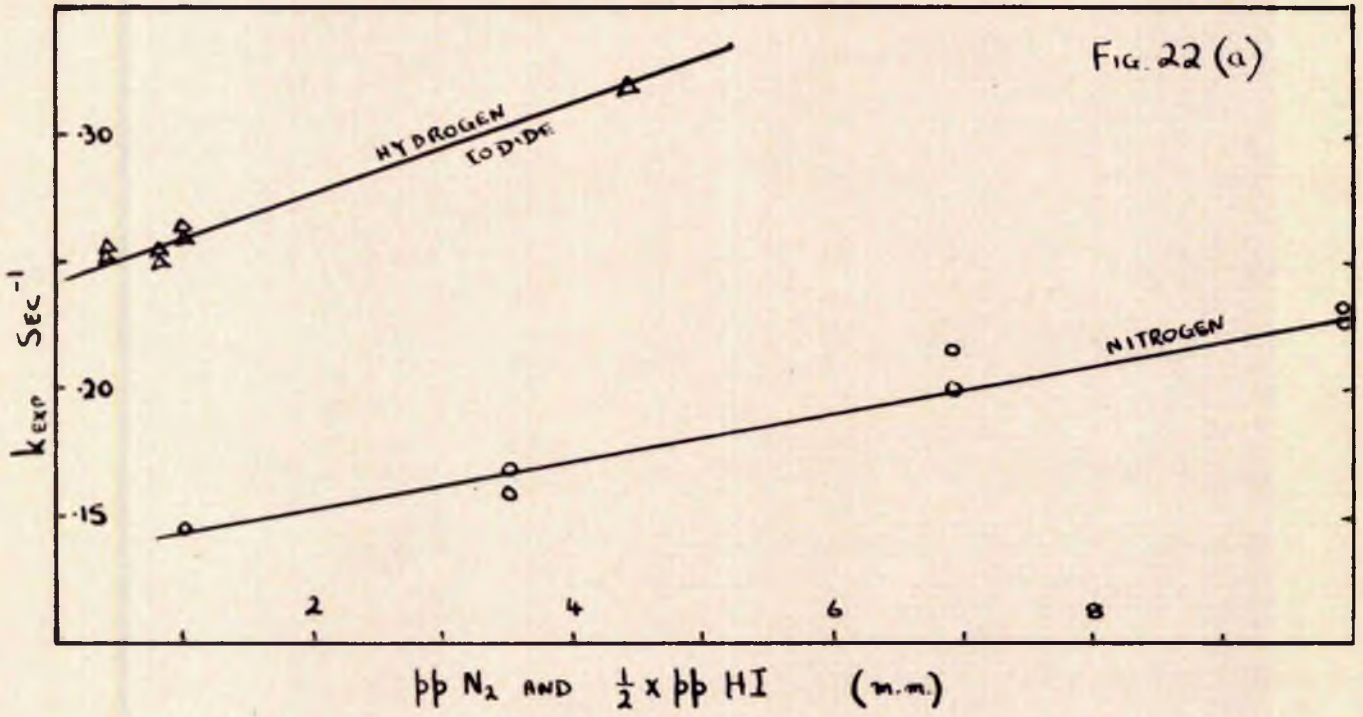
In the preceding section a qualitative picture of the relative efficiencies of the four inert gases viz. nitrogen, hydrogen iodide, benzene and methyl iodide, has been presented. It is, however, possible to express these efficiencies quantitatively with reference to the efficiency of the benzyl iodide molecule itself.

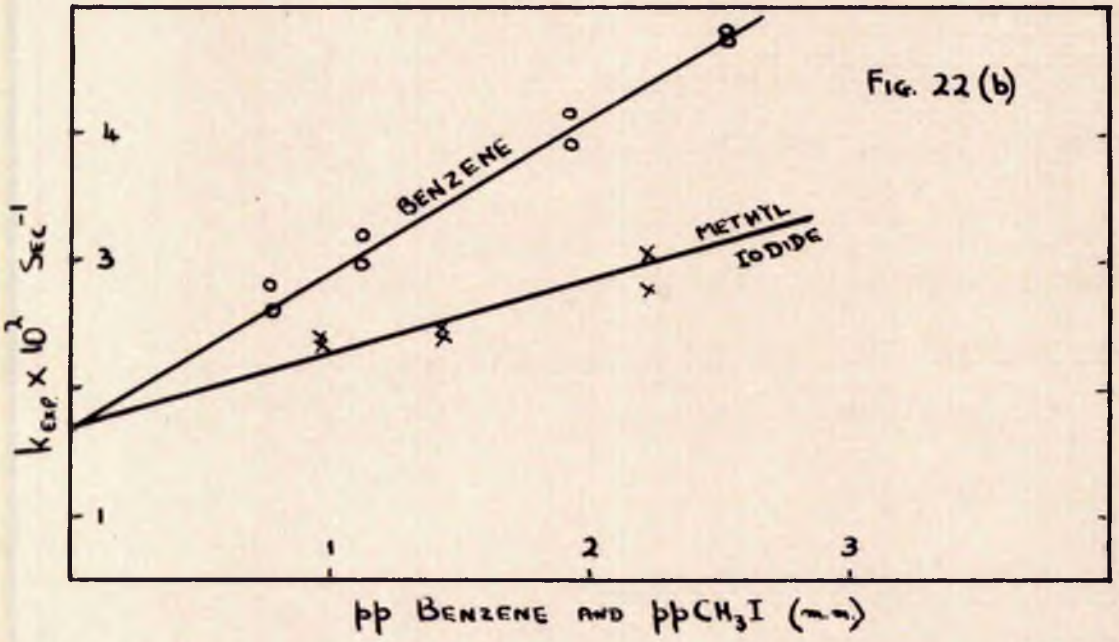
In the original development of the Hinshelwood-Lindemann mechanism, it was assumed that the reactant was activated by other reactant molecules only and no account was taken of the part played by the other molecules present. A development of the original theory allows the efficiency of inert gases, in transferring energy to the reactant molecules, to be calculated. Such a development has been given by Johnston[87] in a series of papers. The reasoning used by Johnston is described in Appendix 2 and it will suffice here merely to give his final equation which is;

$$k = k_1(A) + k_{1X}(X) + k_{1Y}(Y) \qquad (4)$$

where k = experimental rate constant for assumed first order reaction

k_1 = rate constant for $A + A \longrightarrow A^* + A$





FIGS. 22(a) AND 22(b). VARIATION OF ASSUMED FIRST ORDER RATE CONSTANT WITH THE PARTIAL PRESSURE OF VARIOUS INERT GASES.

k_{1X} = rate constant for $A + X \longrightarrow A^* + X$

k_{1Y} = rate constant for $A + Y \longrightarrow A^* + Y$

The efficiency of an inert gas X in transferring energy to the reactant A, relative to the efficiency of A itself, is obviously given by $\alpha_X = \frac{k_{1X}}{k_1}$. It should be emphasised that equation (4) only holds in the second order region i.e. at low partial pressures.

From equation (4) it is evident that a graph of k against (X) at a fixed benzyl iodide concentration should be a straight line of slope k_{1X} and intercept k (BzI). When there are two or more inert gases present at the same time, if only one of them, (X), is varied, then the intercept becomes $k(BzI) + k_{1Y}(Y) \ldots\ldots$ or $k_1 \left[(A) + \alpha_Y(Y) \ldots\ldots \right]$ and therefore $\alpha_X = \frac{\text{slope}}{\text{intercept}} \times \left[(A) + \alpha_Y(Y) \ldots\ldots \right]$. Plots of assumed first order rate constants versus pressures of nitrogen, hydrogen iodide (in the region where there is no reverse reaction), benzene and methyl iodide are shown in Figures 22a and 22b. In each case, a reasonably straight line graph is obtained. Unfortunately all four of the gases were not investigated at the same temperature but, if we assume that the relative efficiency of inert gas molecules is independent of temperature over the short range involved, then it is possible to evaluate α_{N2}, α_{HI}, α_{Ph-H}, and α_{CH_3I}. Since there is always at least two of the gases present (nitrogen and hydrogen iodide), a pair of simultaneous equations must be solved to give α_{HI} and α_{N2}. The values of these can then be used to calculate the relative efficiencies of benzene and methyl iodide. Using the results in Figures 22a and 22b the following values are obtained:-

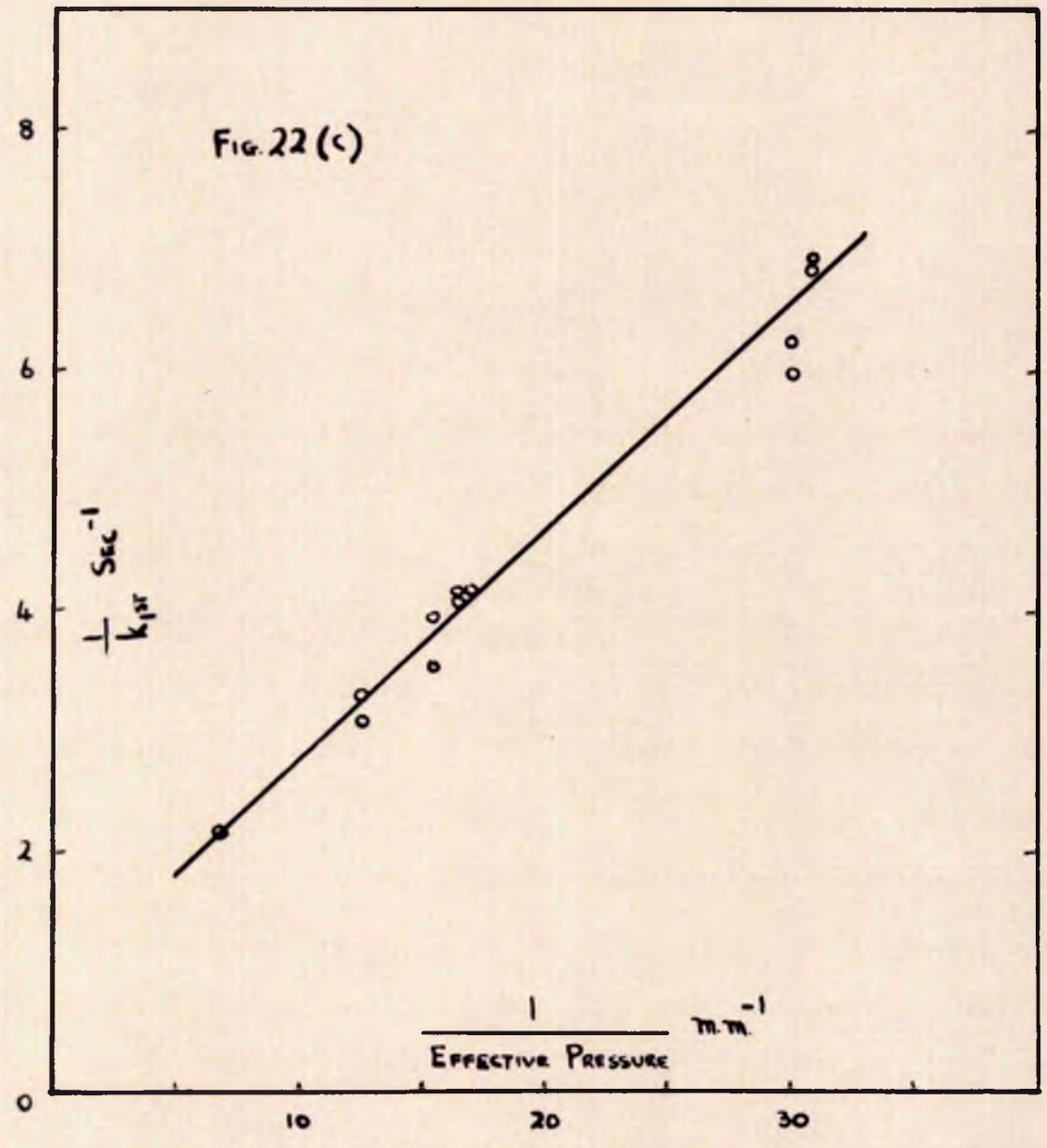


Fig. 22 (c). Reciprocal of First Order Rate Constant

v.

Reciprocal of Effective Pressure.

α_{N_2} = .003

α_{HI} = .008

$\alpha_{Ph.H}$ = .012

α_{CH_3I} = .004

As would have been expected benzene is the most effective of the gases and nitrogen the least. However, even the value for benzene is much lower than the efficiencies quoted in the literature e.g. 0.07 for α_{N_2} and 1.10 for $\alpha_{Ph.H}$ in the decomposition of cyclo-propane.

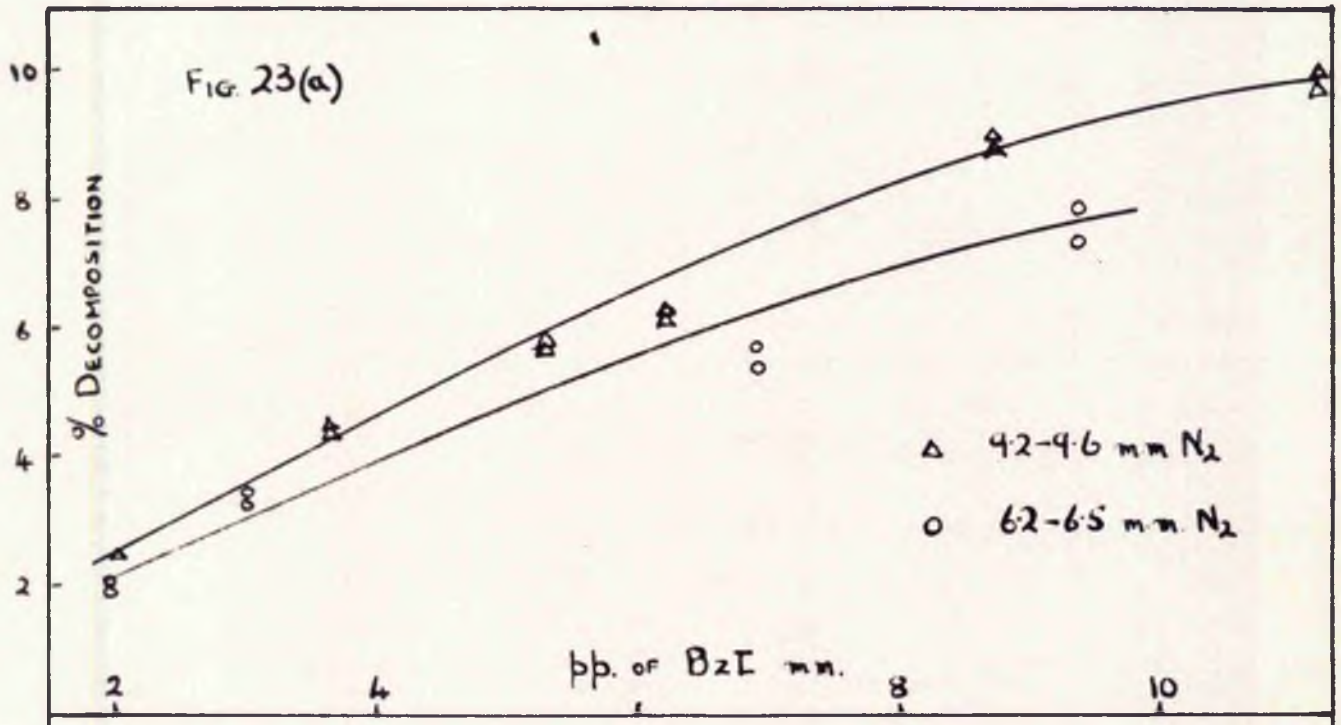
2.7 VARIATION OF BENZYL IODIDE PRESSURE AT DIFFERENT NITROGEN PRESSURES

A further consequence of the Lindemann theory of unimolecular reactions (see Appendix 2) is that a graph of the reciprocal of an assumed first order rate constant against the reciprocal of 'effective' pressure should be a straight line. The 'effective' pressure is defined as the partial pressure of reactant plus the effective partial pressures of the other gases present i.e. in this case equal to p.p. BzI + $\alpha_{N_2} \times$ p.p. N_2 + $\alpha_{HI} \times$ p.p. HI. Using the values of α_{N_2} and α_{HI} derived in the previous section, it is possible to use the results in Section 2.4 to construct such a graph. The calculations are shown in Table 16 and in Figure 22c. The fact that Figure 22c is a reasonable straight line would seem to indicate that the reaction is a unimolecular one proceeding according to the Hinshelwood-Lindemann mechanism.

Table 16

Experiment No.	Assumed 1st. order rate const. $sec.^{-1}$	$\frac{1}{k_{1st.}}$ sec.	Effective pressure mm.	$\frac{1}{\text{Eff. pressure}}$ mm^{-1}
135	.146	6.85	.0326	30.7
136	.144	6.95	.0326	30.7
138	.166	6.0	.0334	30.0
139	.160	6.25	.0334	30.0
141	.253	3.95	.0647	15.5
142	.282	3.55	.0647	15.5
144	.304	3.30	.0862	12.5
145	.326	3.07	.0862	12.5
153	.464	2.15	.150	6.67
121	.240	4.16	.059	17.0
122	.238	4.20	.059	17.0
126	.248	4.04	.060	16.7
127	.244	4.10	.060	16.7

In an attempt to give further support to this, two series of experiments, with 6.2-6.5 mm. and 9.2-9.6 mm. of nitrogen respectively, were carried out in which the partial pressure of benzyl iodide was varied. The results are given in Table 17 - the percentage decompositions having been corrected to 0.71 sec. reaction time.



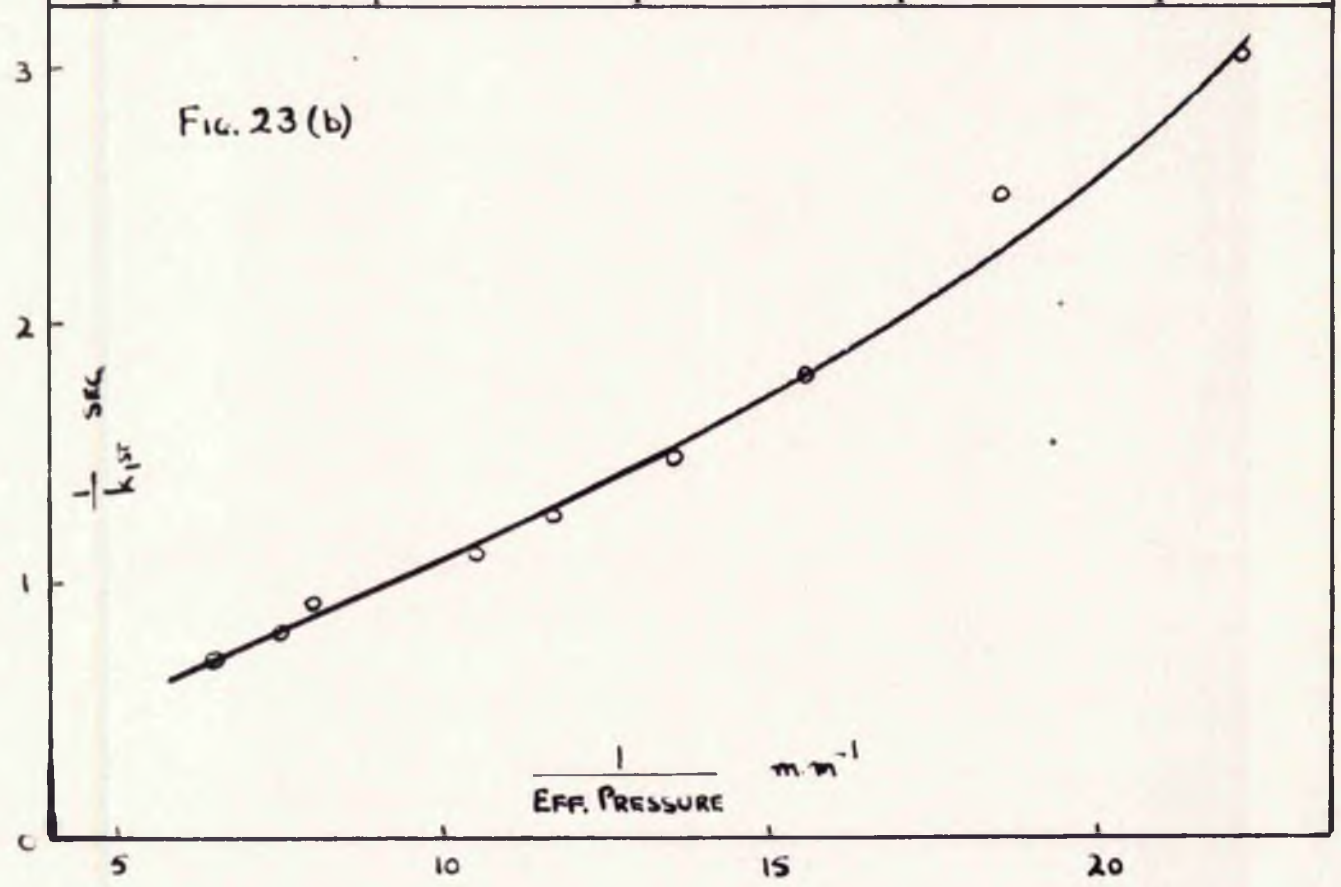


FIG 23 (a) % DECOMPOSITION V. pp. of BzI AT DIFFERENT pp's OF N_2

FIG 23 (b) $\frac{1}{\text{1ST ORDER RATE CONSTANT}}$ V. $\frac{1}{\text{EFF. PRESSURE}}$

Table 17

Temperature 554-555°K

Experiment No.	Reaction time secs.	p.p. BzI mm.	p.p. HI mm.	p.p. N_2 mm.	Corrected % decomp.
183	.71	.069	.77	6.3	5.4
184	.71	.069	.77	6.3	5.7
186	.71	.030	.815	6.3	3.3
187	.71	.030	.815	6.3	3.5
189	.75	.0191	.847	6.2	2.1
190	.75	.0191	.847	6.2	1.9
213	.78	.0936	.835	6.5	7.9
214	.78	.0936	.835	6.5	7.4
192	.68	.020	.788	9.5	2.5
193	.68	.020	.788	9.5	2.5
195	.71	.0618	.790	9.4	6.1
196	.71	.0618	.790	9.4	6.3
198	.70	.0366	.794	9.6	4.5
200	.70	.0366	.794	9.6	4.5
201	.69	.0872	.810	9.4	8.9
202	.66	.0872	.810	9.4	9.1
204	.75	.113	.860	9.2	9.7
205	.75	.113	.860	9.2	10.0
207	.73	.053	.850	9.5	5.7
208	.73	.053	.850	9.5	5.8

These results are illustrated in Figure 23a. Using values of the percentage decomposition at various partial pressures of benzyl iodide from Figure 23a, the corresponding values of $\frac{1}{k_{1st.\ order}}$ and $\frac{1}{\text{Effective pressure}}$ can be calculated (the values $\alpha_{N_2} = 0.003$ and $\alpha_{HI} = 0.008$ obtained in Section 2.6 being used). The results obtained from such calculations are shown in Table 18.

Table 18

Average p.p. N_2	p.p. BzI mm.	Eff. p. mm.	$\frac{1}{\text{Eff. p. mm.}^{-1}}$	$k_{1st.\ order}$ sec.$^{-1}$	$\frac{1}{k_{1st.\ order}}$ sec.
6.3 mm.	.020	.045	22.2	.324	3.08
	.040	.065	15.4	.550	1.82
	.060	.085	11.7	.790	1.27
	.100	.125	8.0	1.09	.920
4.3 mm.	.020	.0545	18.4	.396	2.53
	.040	.0745	13.4	.672	1.49
	.060	.0945	10.6	.905	1.11
	.10	.1345	7.45	1.30	0.77
	.120	.1545	6.50	1.48	0.68

The reciprocal of the assumed first order rate constant has been plotted against the reciprocal of the effective pressure in Figure 23b. This graph, while approximating to a straight line at the higher pressures, shows distinct deviations from this behaviour at the lowest pressures studied. At these low pressures of benzyl iodide and relatively high pressures of nitrogen, the value of the term $\alpha_{N_2} \times p_{N_2}$ is of the same order of magnitude as the partial pressure of the benzyl iodide itself and therefore the calculations will be very sensitive to errors in the experimentally determined value of α_{N_2}.

2.8 VARIATION OF REACTION RATE WITH TEMPERATURE

In the foregoing sections it has been suggested that the decomposition of benzyl iodide in the presence of an excess of hydrogen

iodide is unimolecular but the reaction is not first order because of the very low partial pressures employed - in fact, the reaction is apparently close to second order at the lowest pressures of benzyl iodide used. It should be possible, therefore, by working in the region of 0.02 mm. pressure of benzyl iodide, to determine the variation of the second order reaction rate constant with temperature. In Table 19, the results of experiments at temperatures in the range 534°-596°K are collected. The second order rate constants shown in the Table have been calculated using the expression

$$k_{2nd.\ order} = \frac{1}{t} \cdot \frac{x}{a(a-x)} \quad 1\ mole^{-1}\ sec.^{-1}$$

where x = moles/l of iodine

a = initial (BzI) in moles/l

t = reaction time in secs.

Table 19

N_2 Pressure 3.6-3.8 mm.

HI Pressure 0.19-0.25 mm.

Exp. No.	Temp. °K	Reaction Time secs.	p.p. BzI mm.	% Decomp.	Second order rate constant $k_2 \times 10^{-5}$	log k_2
138	585	.57	.020	9.0	3.24	5.510
139	585	.57	.020	8.7	3.14	5.497
165	596	.58	.0168	15.7	7.04	5.848
166	596	.58	.0168	16.1	7.26	5.861
168	565	.61	.0166	3.4	1.24	5.093
169	565	.61	.0166	3.6	1.29	5.111
171	554	.71	.020	2.1	0.501	4.700
172	554	.71	.020	2.2	0.525	4.720
174	544	.89	.0188	1.5	0.314	4.497
175	544	.89	.0188	1.6	0.316	4.500
177	534	.95	.0186	0.58	0.111	4.045
178	534	.95	.0186	0.56	0.107	4.029

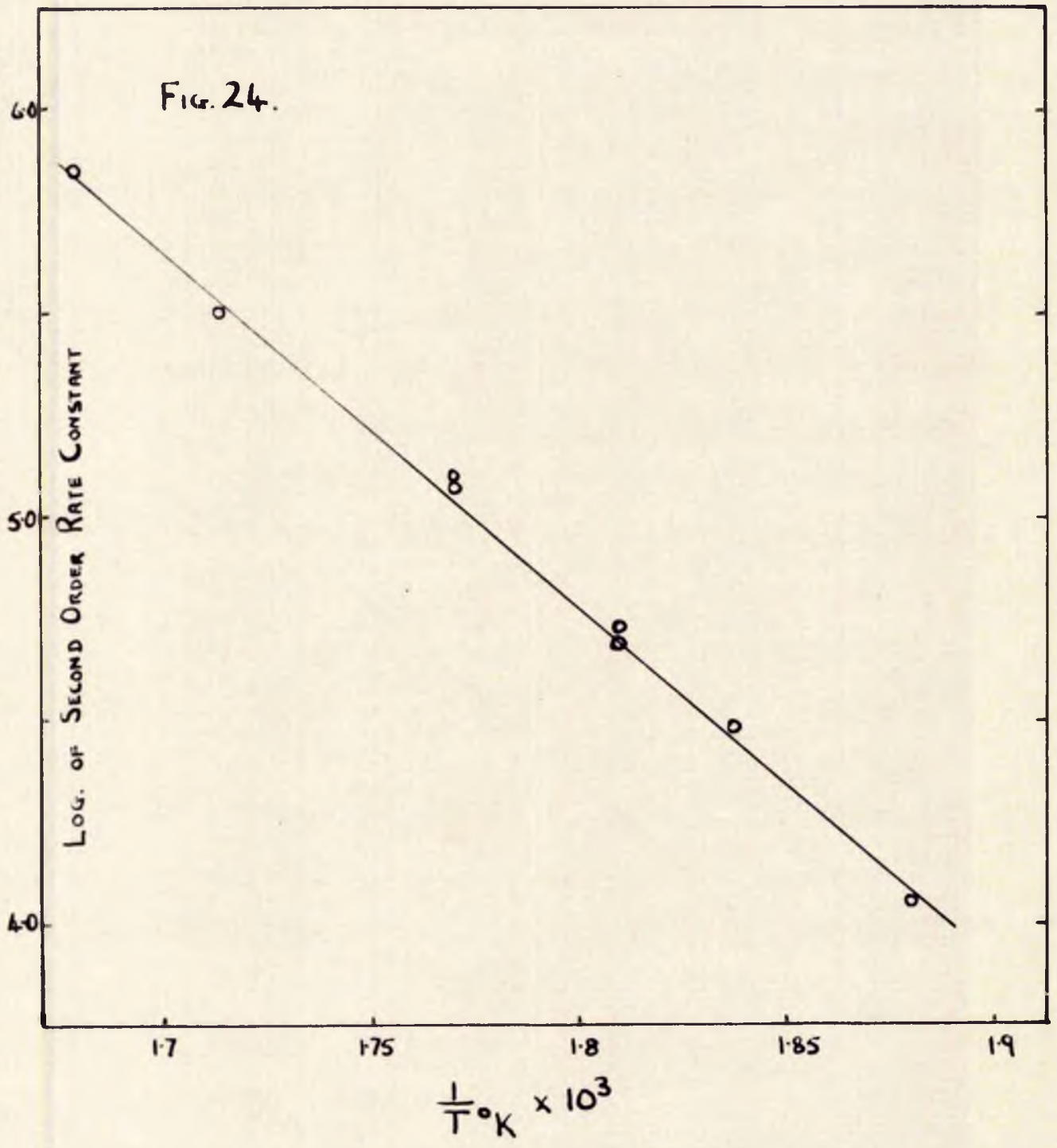


FIG. 24. LOG. OF SECOND ORDER RATE CONSTANT v. $\frac{1}{T°K}$

If the reaction is second order for the reasons outlined, then a plot of the logarithm of the second order rate constant against the reciprocal of the absolute temperature should lead to an activation energy which is equivalent to the energy required to be gained by a benzyl iodide molecule before it can decompose. The results in Table 19 have been used to construct Figure 24 and from the latter, the activation energy may be calculated as 40 K cal./mole. This activation energy should, in fact, be the benzyl iodide bond strength, provided the kinetic interpretation is correct, and as such it appears to be excellent confirmation of the results obtained from the experiments described in Section 1. (In Section 1 it was shown that the bond strength probably lay between 40 and 42 K cal./mole).

The Arrhenius factor B, in the expression $k_{2nd.\ order} = Be^{-E/RT}$ can be calculated from Figure 24 as $10^{20.4}$. The simple collision theory for bimolecular reactions predicts that the collision frequency will be of the order of only 10^{11} l mol.$^{-1}$ sec.$^{-1}$. However, the type of reaction, involved in this particular case, is the activation by collision of a benzyl iodide molecule and, since the molecule is a complex one, this process might be expected to proceed at a rate in excess of that predicted by the simple collision theory. The rate of activation of a complex molecule can be much higher than that for a simple one since the probability that it has an energy greater than E is $(\frac{E}{RT})^{n-1} \cdot \frac{1}{(n-1)!} \cdot e^{-\frac{E}{RT}}$ whereas for a simple molecule it is merely $e^{-\frac{E}{RT}}$, n being the number of vibrational degress of freedom which can contribute to the activation energy. Even such a simple molecule as fluorine monoxide[88] has been shown to have a second order

decomposition rate which obeys the expression $k = 10^{19.7} \times \exp.(-39000/RT)$ 1 $mol.^{-1}$ $sec.^{-1}$. At this stage in the investigation, it therefore seemed not at all unreasonable that benzyl iodide should have a pre-exponential factor as high as 10^{20} in the second order region.

3. THE DECOMPOSITION OF BENZYL IODIDE IN THE PRESENCE OF HYDROGEN IODIDE AND FREE IODINE

3.1 INTRODUCTION

Although the results in Section 2 appear to substantiate the theory that the decomposition of benzyl iodide, in the presence of hydrogen iodide is undergoing a first to second order transition in accordance with the tenets of the Hinshelwood-Lindemann theory, there are two major difficulties preventing the complete acceptance of this hypothesis viz.

(a) the experimental values of the efficiencies of the various inert gases are very much lower than those found by other workers.

(b) if the bond strength of benzyl iodide is approximately 42 K cal./mol., as given by the results in Section 1, then, using an Arrhenius factor of 10^{13}, the first order rate constant at 554.4°K may be calculated as 2.5×10^{-4} sec.$^{-1}$. This value is about a thousand times less than that suggested by the results in Table 17. Thus, if the reaction is genuinely in the first to second order transition region, then the decomposition rate must have an abnormally high pre-exponential factor under first order conditions.

Gazith and Noyes[23], in their study of the exchange reaction between iodine and benzyl iodide in solution, postulate the reaction step $I + BzI \longrightarrow Bz + I_2$ and it is possible that such a reaction also

takes place in the gas phase. It was shown in Section 1 that a consistent kinetic analysis was obtained by assuming that the rate of decomposition of benzyl iodide was governed by the equilibrium $BzI \overset{Ke}{\longleftrightarrow} Bz + I$ followed by the recombination of iodine atoms. It should, perhaps, be pointed out that this is technically equivalent to assuming that the equilibrium $I + BzI \overset{Ke^*}{\longleftrightarrow} Bz + I_2$ is established, since the equilibrium constants, for these two processes, are related by the expression $Ke^* = \frac{Ke}{K_{I_2}}$, where K_{I_2} is the equilibrium dissociation constant of iodine.

If an iodine atom-benzyl iodide reaction of this type does occur, the addition of iodine to the system should increase the rate of decomposition of benzyl iodide when an excess of hydrogen iodide is present. This is precisely the opposite 'iodine effect' to that found for the decomposition in the absence of a radical acceptor. The occurrence of an iodine dependent reaction of this type could, however, explain the difficulties encountered in attempting to reconcile the experimental results in Section 2 with the theories of unimolecular reactions. For example, it would explain why the inert gas efficiencies, obtained in Section 2.6, are very low, since the inert gas would only be expected to affect the initial dissociation reaction of the benzyl iodide and not the iodine catalysed reaction. It is also probable that the initial dissociation does not, in fact, take place in the truly second order region, thus invalidating the inert gas efficiency equations which were used.

3.2 VARIATION OF REACTION RATE WITH CONCENTRATION OF ADDED IODINE

A few experiments, at constant temperature and constant partial pressures of benzyl and hydrogen iodides, were performed in which different amounts of free iodine were added to the system. These results are given in Table 20 - the percentages of decomposition have been corrected in the usual way for slight variations in the reaction time and in the partial pressure of benzyl iodide.

Table 20

Temperature 574°K

Exp. No.	Reaction time secs.	p.p. BzI mm.	p.p. HI mm.	p.p. I_2 added mm. x 10^3	Corrected % decomp. (.5 sec. and .016 mm.)
292	.51	.0169	0.57	-	5.55
293	.51	.0169	0.57	2.16	7.80
294	.51	.0169	0.57	2.16	7.70
296	.51	.0156	0.60	2.92	7.82
297	.51	.0156	0.60	2.92	8.21
298	.49	.0146	0.61	-	5.68
299	.49	.0146	0.61	5.56	9.06
300	.49	.0146	0.61	5.56	8.90

From Table 20, it is immediately evident that the addition of iodine results in a considerable increase in the rate of decomposition. If this increase in rate is due to the occurrence of a reaction involving the attack of an iodine atom on the organic iodide molecule, then the overall decomposition rate can be represented by an equation of the type

$$\frac{dI_2}{dt} = M_1 (BzI) + M_2 (BzI)(I)$$

where M_1 and M_2 are constants. Thus a graph of the rate of iodine production against the iodine atom concentration, at constant benzyl iodide concentration, should be a straight line whose slope is given by M_2 (BzI) and whose intercept on the (I) = 0 axis is M_1 (BzI). Although actual values of the iodine production rate and the iodine atom concentration at any instant are not known, it is possible to calculate their approximate mean values from the results in Table 20. The mean rate of iodine formation may be calculated directly but calculation of the corresponding mean iodine atom concentration is not quite so straight-forward. Measurement of the total iodine present at the entry of the reaction zone enables the concentration of iodine atoms there to be calculated, if the fraction dissociated is known. The degree of dissociation can be obtained from data on the equilibrium dissociation constants for iodine by the method described in Section 1. Because the temperatures used in this series of experiments were very much lower than those at which Perlman and Rollefson studied the equilibrium dissociation of iodine, it was thought inadvisable to use a simple extrapolation of their results. Instead the formula $\log K_p = - \frac{35,514}{4.57\ T} + .935 \log T + 2.44$ computed by Downs[7], using Perlman and Rollefson's[78] data, has been used. In an exactly similar way, the iodine atom concentration at the exit of the reaction zone may be calculated. The arithmetic mean of the initial and final values should give a reasonable measure of the effective average iodine atom concentration.

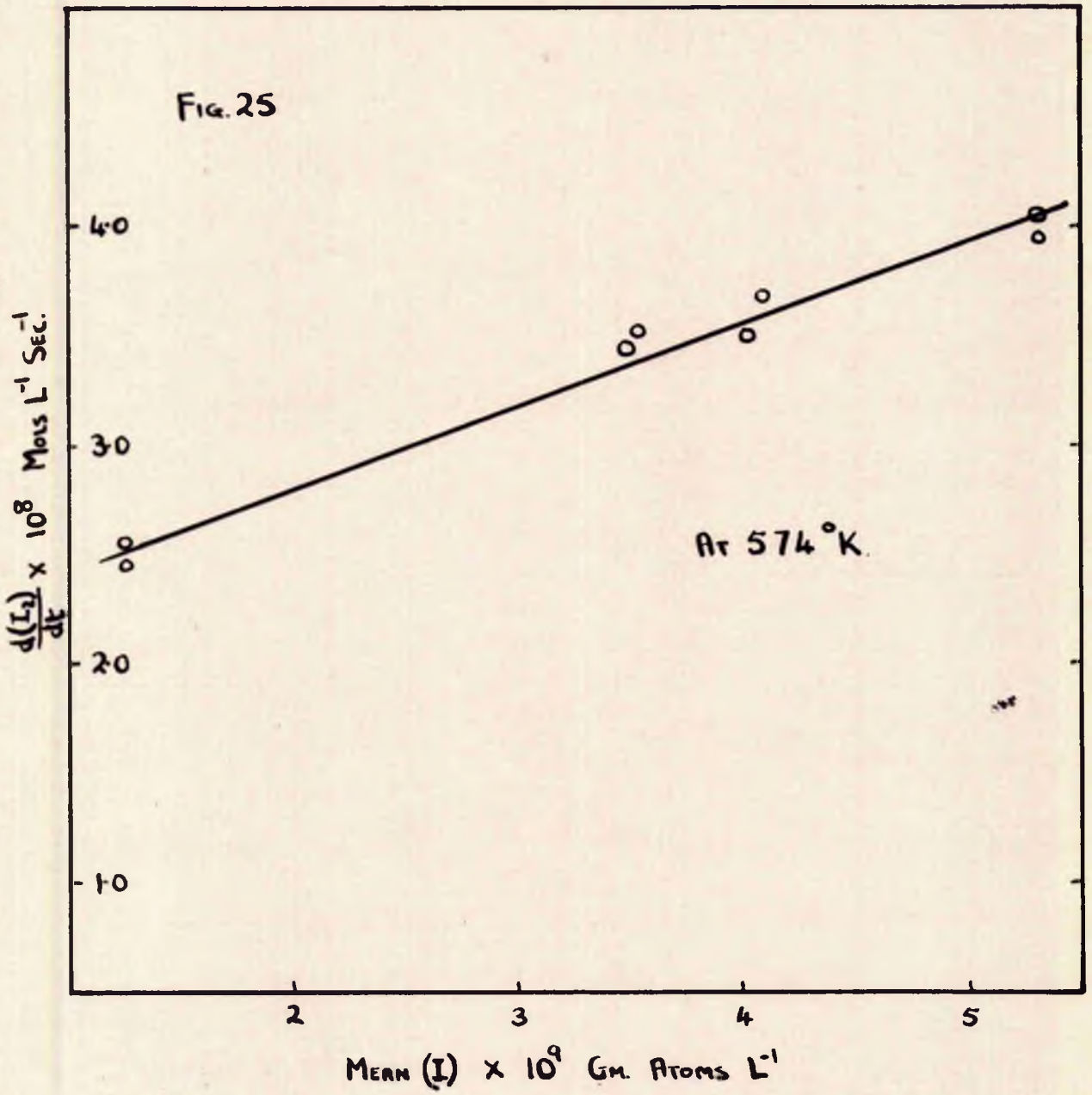


FIG. 25. RATE OF FORMATION OF I_2 V. MEAN (I)

Values of the mean rates of iodine production and the mean iodine atom concentrations for experiments 292-300 have been calculated and the results are given in Table 21.

Table 21

Variation of $\frac{dI_2}{dt}$ with (I) at 574°K

Exp. No.	p.p. BzI mm.	(I) x 10^9 Initial	(I) x 10^9 Final	Mean (I) x 10^9	Mean $\frac{dI_2}{dt}$ x 10^8 at 0.016 mm. BzI
292	.0169	0.0	2.51	1.25	2.48
293	.0169	2.77	4.30	3.53	3.5
294	.0169	2.77	4.28	3.48	3.47
296	.0156	5.53	4.54	4.03	3.5
297	.0156	3.53	4.67	4.10	3.67
298	.0146	0.0	2.50	1.25	2.55
299	.0146	4.74	5.85	5.29	4.05
300	.0146	4.74	5.80	5.29	3.95

(I) are expressed in gm. atoms l^{-1} and $\frac{dI_2}{dt}$ in mols. l^{-1} sec.$^{-1}$

Figure 25 illustrates that, at constant benzyl iodide pressures, the rate of iodine production is directly proportional to the mean iodine atom concentration and from the graph M_1 and M_2 may be calculated as 4.48×10^{-2} sec.$^{-1}$ and 0.89×10^7 l sec.$^{-1}$ gm. atom^{-1} respectively.

3.3 TEMPERATURE DEPENDENCE OF THE IODINE DEPENDENT DECOMPOSITION RATE

In the previous section, the constant M_2 in the expression $\frac{d(I_2)}{dt} = M_1 (BzI) + M_2 (BzI)(I)$ has been evaluated at 574°K.

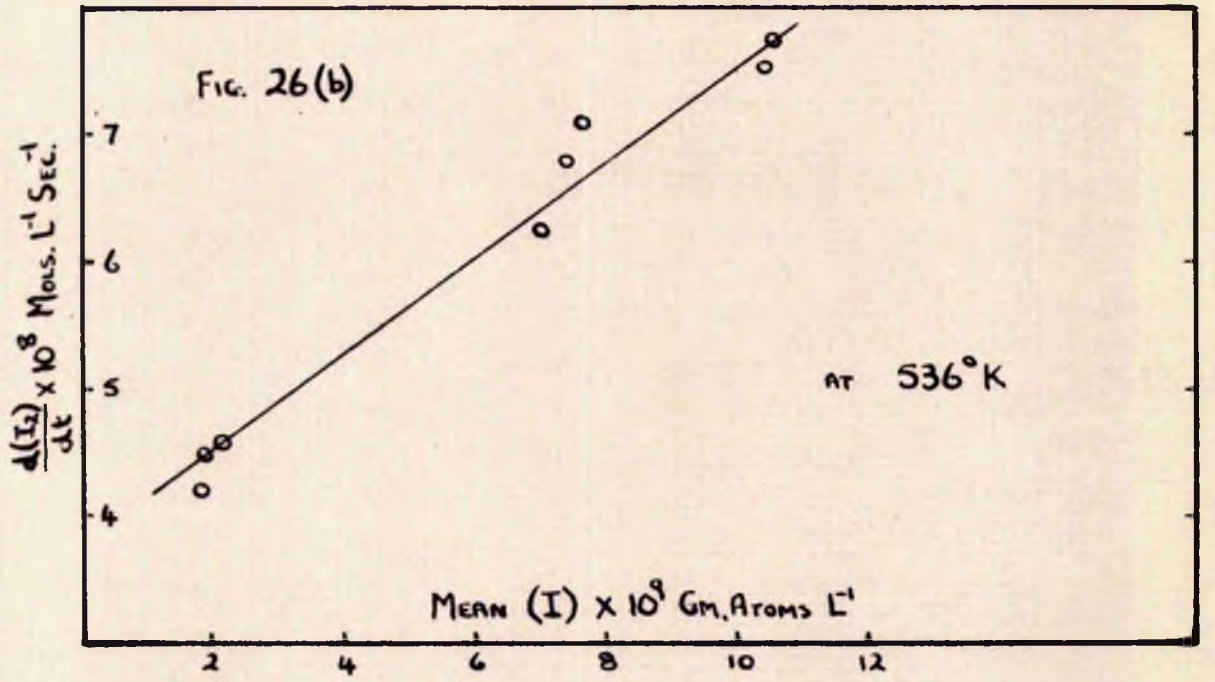


Fig. 26(a). $\frac{d(I_2)}{dt}$ v. Mean (I) at 585°K.

Fig 26(b) $\frac{d(I_2)}{dt}$ v. Mean (I) at 536°K.

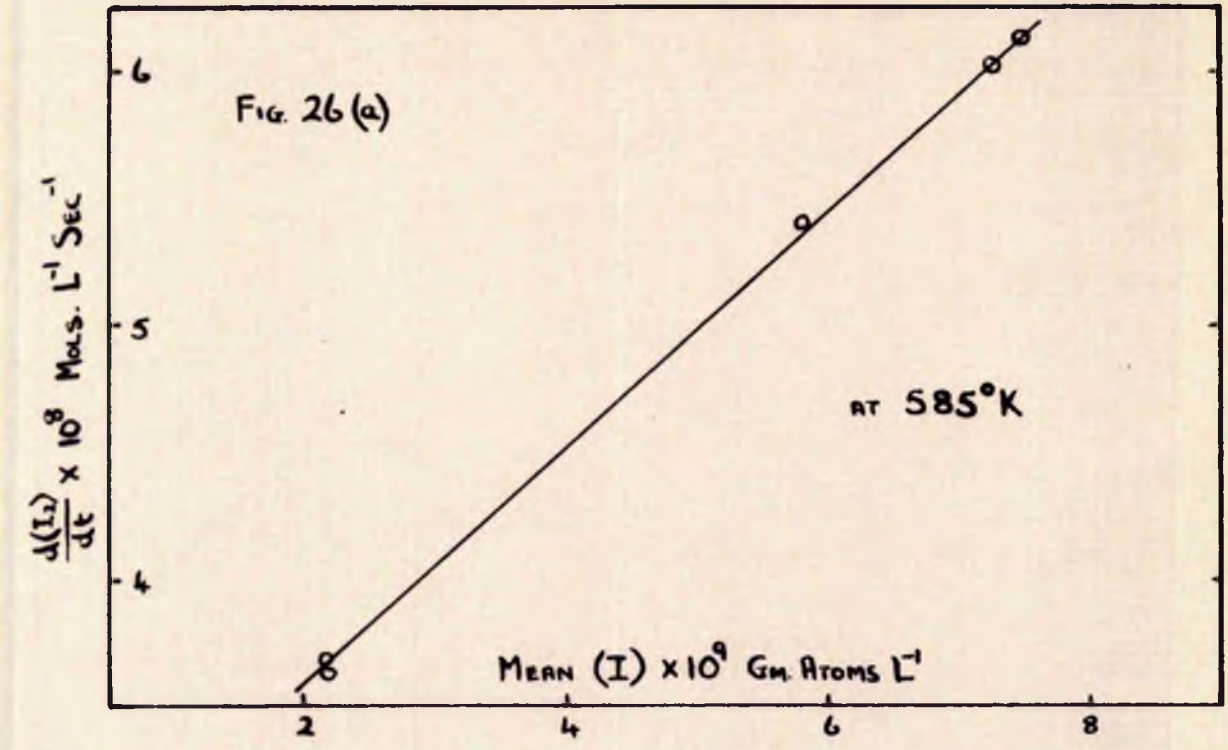


FIG. 26 (a)
$\frac{d(I_2)}{dt} \times 10^8$ MOLS. L^{-1} SEC^{-1}
6
5
4
AT 585°K
MEAN (I) $\times 10^9$ GM. ATOMS L^{-1}
2
4
6
8

Similar studies have been made of the iodine atom dependence of the decomposition rate at 585°, 536° and 505°K. The results of these experiments, calculated on the same basis as those in Table 21, are given in Table 22.

Table 22

Exp. No.	Temp. °K	p.p. BzI mm.	(I) x 10^9 initial	(I) x 10^9 final	(I) x 10^9 mean	Mean $\frac{dI_2}{dt}$ x 10^8 at 0.016 mm. BzI
302	585	0.0152	0	4.35	2.17	3.67
303	585	0.0152	4.4	7.28	5.84	5.40
304	585	0.0154	0	4.25	2.12	3.64
305	585	0.0154	6.91	8.05	7.48	6.25
306	585	0.0154	6.91	7.80	7.36	6.03
307	536	0.0157	0	0.357	0.178	0.423
308	536	0.0157	0.975	1.13	1.05	0.775
309	536	0.0157	0.975	1.10	1.04	0.755
310	536	0.0172	0	0.409	0.204	0.460
311	536	0.0172	0.70	0.827	0.743	0.680
312	536	0.0172	0.70	0.842	0.771	0.715
313	536	0.0161	0	0.380	0.190	0.451
314	536	0.0161	0.650	0.761	0.705	0.622
315	505	0.0152	1.42	1.56	1.49	0.40
316	505	0.0152	1.42	1.58	1.50	0.425

As previously, the iodine atom concentration is expressed in gm. atom l^{-1} and the rate of iodine production in mols. l^{-1} $sec.^{-1}$.

The results of the experiments at 585°K and 536°K are shown in Figures 26a and 26b respectively. From these two graphs, M_2 may be calculated as 1.01 x 10^7 and 7.36 x 10^6 l $sec.^{-1}$ gm. atom $^{-1}$ at 585° and

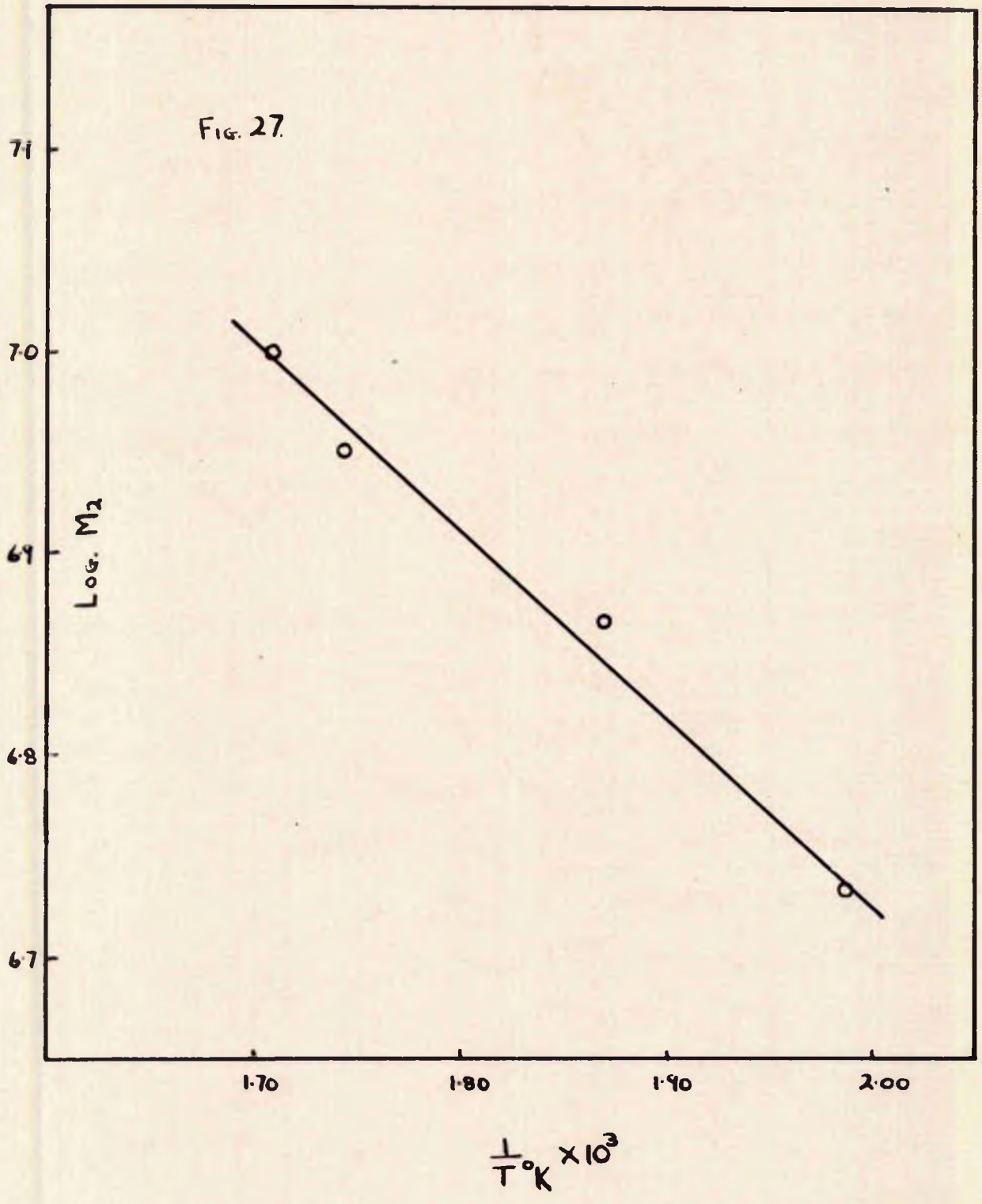


Fig. 27. Logarithm of M_2 v. $\frac{1}{T°K}$.

536°K respectively. At 505°K, no detectable reaction took place in the absence of added iodine and thus it may be assumed that the M_1(BzI) term is zero. This leads to a mean value of 0.535×10^7 l sec.$^{-1}$ gm. atom^{-1} for M_2. The term M_2 is in effect the rate constant in the reaction $I + BzI \longrightarrow Bz + I_2$ and therefore a graph of log M_2 against the reciprocal of the absolute temperature should yield the energy of activation of this reaction. The required Arrhenius plot is shown in Figure 27 from which the energy of activation may be calculated as 4.1 K cal./mol. and the corresponding pre-exponential factor as $10^{9.3}$ i.e. a steric factor of approximately 10^{-2} is involved.

The accuracy of the above determination is limited by two major factors

(a) The assumption that the arithmetic mean iodine atom concentration is a good approximation for the effective iodine atom concentration may not be justified. Also the implicit assumption that the iodine atom-iodine molecule equilibrium is attained may not be valid.

(b) The relatively small range of temperatures investigated and the limited number of experimental values on each of the $\frac{d(I_2)}{dt}$ versus (I) graphs with the consequent decrease in the accuracy of determining the slopes.

These two factors will now be considered in more detail.

(a) The work of Rabinowitch and Wood[89, 90], on the kinetics of the recombination of iodine atoms, indicates that, under the conditions

of the present experiments, the combination of iodine atoms will be principally a heterogeneous wall reaction and that the limiting rate step will be the diffusion rate to the wall. Iodine atoms, formed in the gas phase from benzyl iodide, will undergo collisions while diffusing to the wall where they will subsequently combine. A formula, given by Bursian and Sorokin[91] (a more detailed discussion of this problem has been given by Semenoff[92]) enables the number of collisions, n, made by a particle in diffusing to the wall of a cylindrical vessel to be calculated. The equation is $n = \frac{3}{32} \frac{d^2}{\lambda^2}$

where d = vessel diameter in cms.

λ = the mean free path in cms.

The mean free path is given by the expression

$$= \frac{1}{\sqrt{2}\ \pi\ m\ \sigma^2}$$

where σ = molecular diameter in cms.

m = number of molecules per cc.

Since the largest proportion of molecules involved in these experiments consisted of nitrogen molecules, it will be assumed that $\sigma = 3.8$ Å, the value for nitrogen. Taking an average value of 0.02 mm. partial pressure of benzyl iodide in a total pressure of 5 mm., then at 550°K, $m = 10^{17}$ molecules/cc. $\sigma^2 = 14.4 \times 10^{-16}$ cms.^{2} and $\lambda = 1.6 \times 10^{-3}$ cms. The diameter of the reaction furnace was 2.5 cms., neglecting the thermocouple well, and n is therefore given by $n = \frac{3}{32} \times \frac{6.25}{2.44 \times 10^{-6}}$

$= 2.4 \times 10^5$ collisions

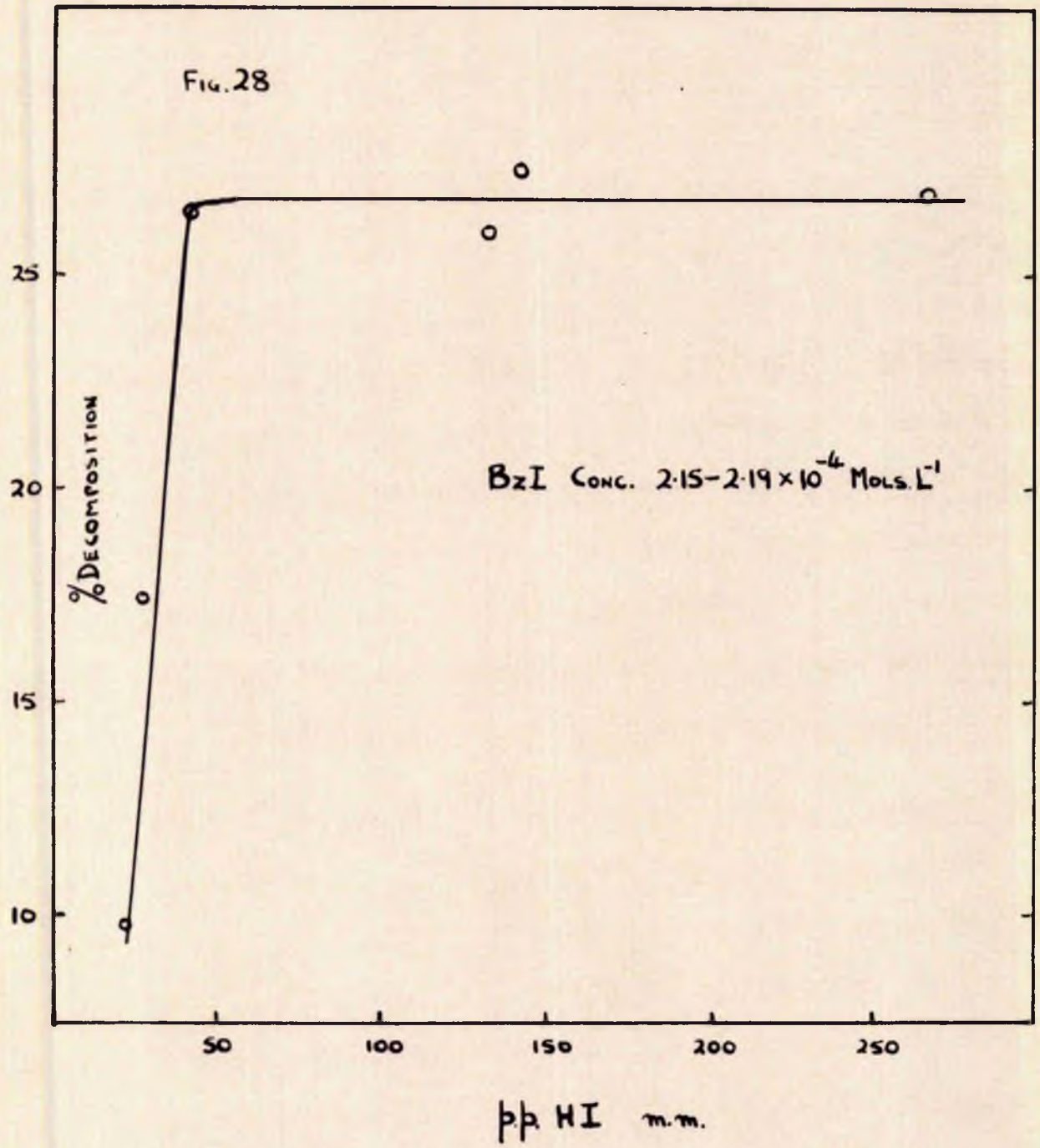


Fig. 28. Static Exp. : % Decomposition v. pp of HI

Thus an iodine atom, in diffusing to the wall, will make this number of collisions with other gas molecules of all kinds. It will therefore collide with $\frac{0.02}{4.0} \times 2.4 \times 10^5$ or 1.2×10^3 molecules of benzyl iodide. The number of collisions between iodine atoms and benzyl iodide molecules which result in reaction is given by:-

No. of fruitful collisions = Total no. of collisions x P x $e^{-E/RT}$

where P is the steric factor of the reaction. The current work suggests a value of 10^{-2} for this steric factor and even lower values were found by Gazith and Noyes[23]. Thus, in order that an atom of iodine should make one fruitful collision with a benzyl iodide molecule before reaching the wall, the energy of activation involved would have to be less than 3 K cal./mol. Experimentally, the activation energy obtained is 4.1 K cal./mol. and therefore the assumption that the iodine atom-iodine molecule equilibrium is established is probably valid.

(b) Attempts were made to increase the accuracy of the value obtained for the activation energy of the reaction by carrying out experiments at much lower temperatures in a static system. As described under 'Apparatus and Experimental Techniques', an oil-filled thermostat was used in these experiments, which were conducted in the region of 100°C. The preliminary experiments were promising and showed that the decomposition rate of benzyl iodide in the presence of hydrogen iodide became independent of the hydrogen iodide pressure as soon as a sufficient excess was present i.e. exactly analogous behaviour to that observed under flow system conditions. Figure 28 shows the type of results obtained. It soon became clear, however, that more benzyl iodide was

being decomposed than could be accounted for by the amount of free iodine formed. This would indicate the formation of more complex reaction products and indeed a solid having a melting point of about 100°C was isolated from the reaction vessels. A cursory examination by ultra-violet and infra-red spectroscopy failed to identify the product, although there were indications that it contained stilbene (mpt. 124°C).

It was noticed that there was apparently some difficulty in getting all of the benzyl iodide into the vapour phase in these sealed bulb experiments and it seems probable that some liquid phase reactions were occurring on the walls of the vessel. (Extrapolation of the available approximate data indicates that the vapour pressure of benzyl iodide at 110°C is not much greater than the partial pressure used in these experiments). Some such liquid phase reactions could account for the formation of stilbene or other more complex products which would be extremely unlikely in a true gas phase reaction at these low temperatures.

Because of these complications, the possibility of extending the temperature range of the investigations of the reaction $I + BzI \longrightarrow I_2 + Bz$, by means of a static system, was not pursued further. If the above explanation of the nature of the complicating reactions is correct, then static experiments, using lower partial pressures of benzyl iodide and thus requiring more refined analytical techniques or the use of much larger reaction vessels, might have been successful.

The determination of the activation energy of the reaction between an iodine atom and a benzyl iodide molecule as 4.1 K cal./mol. enables the bond strength of benzyl iodide to be deduced directly, since the 4.1 K cal./mol. merely represents the difference between the bond strengths

of benzyl iodide and molecular iodine. Since the bond strength of iodine is given by Perlman and Rollefson[78] as 36.5 K cal./mol. at 550°K (the mean of the temperature range investigated), these results are equivalent to a benzyl iodide bond strength of 40.6 K cal./mol., assuming that the reverse reaction Bz + I_2 ⟶ BzI + I has zero energy of activation. This value of 40.6 K cal./mol. is in excellent agreement with that obtained in Section 1 by an entirely different approach.

3.4 EFFECT OF THE "IODINE DEPENDENT REACTION" ON PREVIOUS DATA

At the time at which the experiments discussed in Sections 2.4 to 2.8 were being carried out, it was not realised that a reaction, involving the attack of an iodine atom on the parent molecule, was occurring simultaneously with the normal decomposition reaction. Using the data obtained on the temperature dependence of the rate constant of the reaction BzI + I ⟶ Bz + I_2, the results of previous experiments can be corrected to allow for the occurrence of this reaction. For example, the experiments in Section 2.4 (Table 11), in which the dependence of the overall reaction rate on the benzyl iodide concentration was demonstrated, can now be recalculated to determine the extent of decomposition which is due to the initial dissociation of the benzyl iodide molecule. In the expression $\frac{dI_2}{dt} = M_1(BzI) + M_2(BzI)(I)$, the value of M_2 can be obtained from Figure 27 as 10^7 l gm. atoms^{-1} secs.$^{-1}$ at 585°K and thus the contribution of the term $M_2(BzI)(I)$ can be calculated, using the mean values of the iodine atom concentrations determined as described previously. The results in Table 11 (Section 2.4) have been recalculated, in this way, and the values of the rate of iodine production from the initial

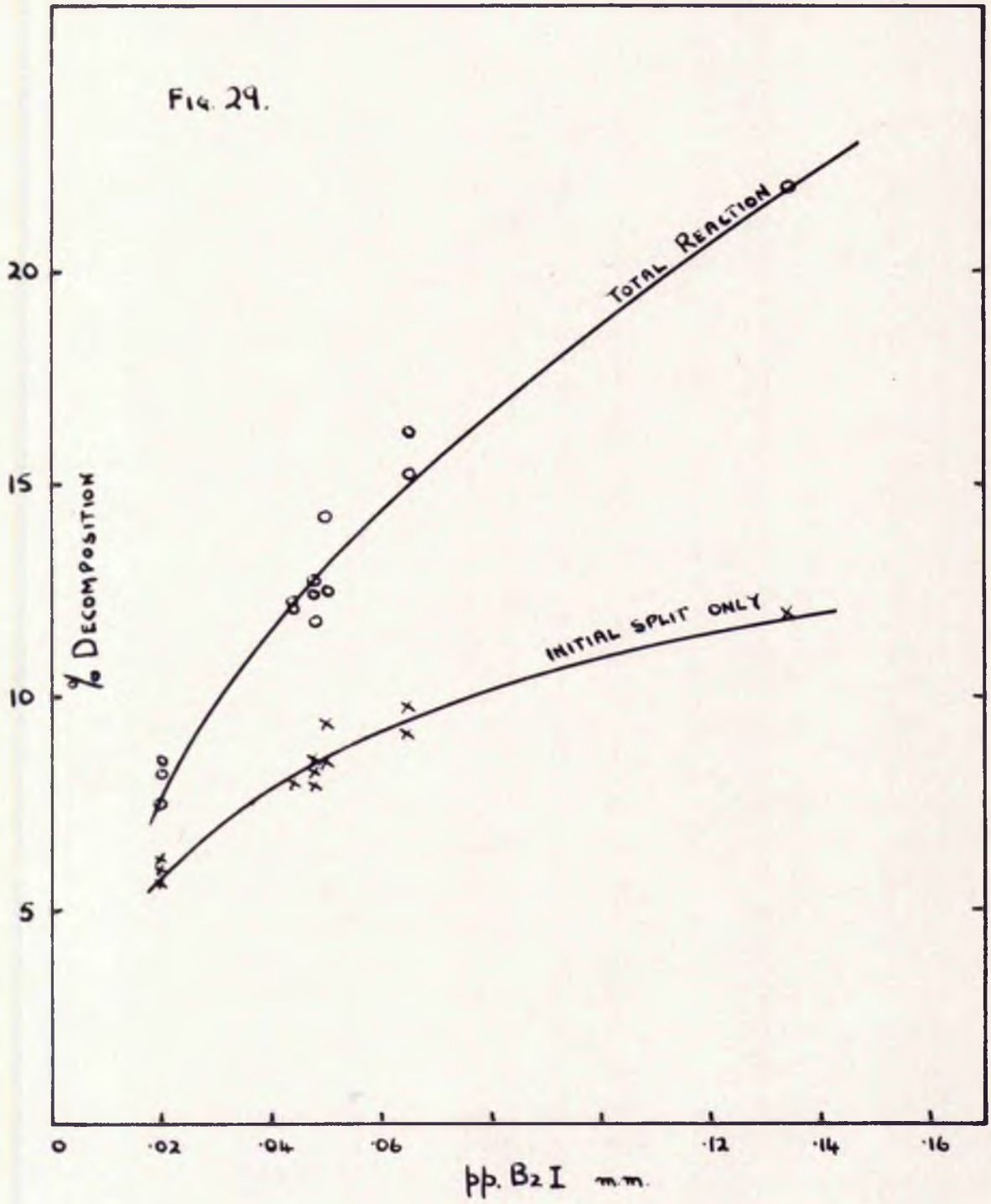


Fig. 29. % Decomposition v. Partial Pressure of B_2I

dissociation only have been obtained and are given in Table 23. From these data, values of the percentage decomposition (at 0.54 secs. reaction time) due only to the initial dissociation, have been calculated - these values being obtained by simple proportion from the values of the rate of iodine production for the overall and the initial dissociation reactions.

Table 23

Exp. No.	p.p. BzI mm.	Mean (BzI) mols./l. x 10^{7}	Total $\frac{dI_2}{dt}$ x 10^{8}	Mean (I) x 10^{9}	$\frac{dI_2}{dt}$ from $I + BzI \rightarrow I_2 + Bz$ x 10^{8}	$\frac{dI_2}{dt}$ from initial dissoc. x 10^{8}	% Decomp. due to initial dissoc. (at 0.54 sec.)
135	.02	5.36	4.2	2.33	1.25	2.95	5.3
136	.02	5.36	4.17	2.31	1.24	2.93	5.3
138	.02	5.31	4.75	2.35	1.25	3.50	6.3
139	.02	5.31	4.25	2.32	1.23	3.02	5.9
121	.044	10.34	13.4	4.32	4.47	8.93	8.1
122	.044	10.34	13.3	4.28	4.44	8.86	8.1
126	.047	11.01	14.8	4.45	4.90	9.90	8.4
127	.047	11.01	14.6	4.37	4.84	9.76	8.3
123	.048	11.28	14.3	4.30	4.85	9.45	7.9
124	.048	11.25	15.1	4.55	5.13	9.97	8.4
141	.050	12.0	16.35	4.55	5.46	10.89	8.5
142	.050	11.9	17.6	4.87	5.92	11.68	9.4
144	.065	15.34	25.25	6.50	9.96	15.29	9.1
145	.065	15.26	26.9	6.95	10.60	16.30	9.8
153	.134	30.43	75.0	11.1	33.8	41.2	12.1

The results in Table 23 are illustrated in Figure 29 on which the original results from Section 2.4 are also shown for comparison. It is evident from the graph that the initial dissociation reaction is considerably less

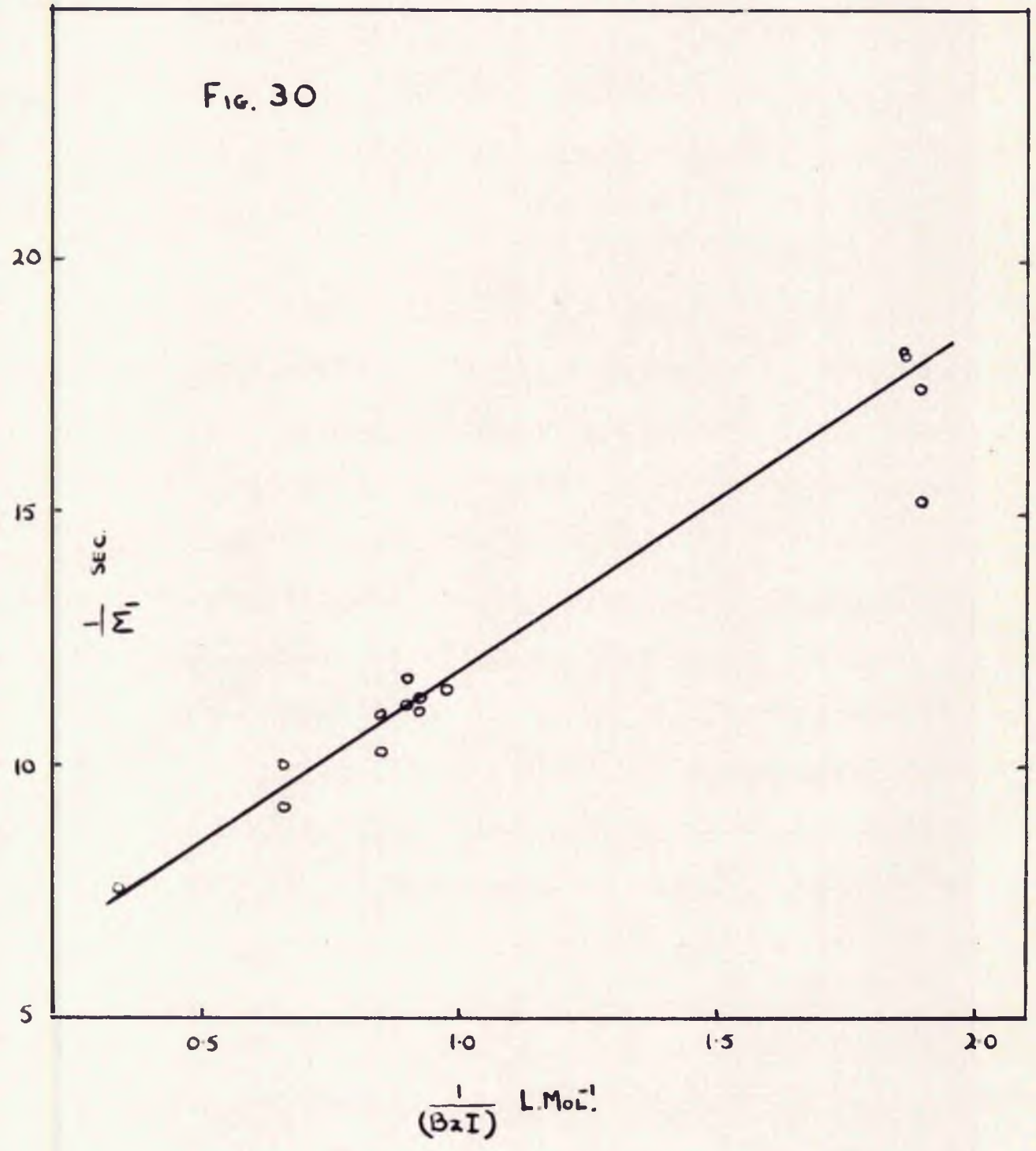


FIG. 30. RECIPROCAL OF M_1 .V. RECIPROCAL OF (BzI)

dependent on benzyl iodide concentration than the overall reaction, particularly at the higher concentrations and it may be that the reaction is not second order even at the lowest pressures used. This latter fact may account for the exceptionally low values of the various inert gas efficiencies obtained (Section 2.6), since the equations used in the calculation of these efficiencies are only valid in the strictly second order region.

It is interesting that the reciprocal of the assumed first order rate constant for the overall reaction when plotted against the "effective pressure" gave a straight line (Section 2.7, Figure 22c), when the results were not entirely due to the effect then assumed. However, for the initial dissociation of benzyl iodide, a graph of $\frac{1}{M_1}$ against $\frac{1}{(BzI)}$ should be a straight line where M_1 is the constant in the rate expression $\frac{dI_2}{dt} = M_1(BzI) + M_2(I)(BzI)$. Table 24 gives the necessary data which are illustrated in Figure 30. The graph, in Figure 30, is a reasonable straight line, despite the fact that no allowance has been made for the effect of inert gases. The value of M_1 at infinite pressure is given by Figure 30 as 0.175 secs.$^{-1}$. Now M_1 is equal to half of the rate constant for the initial dissociation (since $\frac{dI_2}{dt}$ is in mols. l^{-1} secs.$^{-1}$ and two molecules of benzyl iodide must decompose to give one of iodine) and therefore at 585°K, the first order decomposition rate constant, for the initial dissociation of a benzyl iodide molecule, is 0.35 secs.$^{-1}$. If the value of 40.6 K cal./mol. for the activation energy of this decomposition, obtained in Section 3.3, is correct then this value of the rate constant corresponds to an Arrhenius factor of $10^{14.6}$.

This value is at the upper end of the range of Arrhenius factors which are usually considered normal[93].

Table 24

Exp. No.	Mean (BzI) mols. l^{-1} x 10^7	$\frac{1}{(BzI)}$ $mols^{-1}$ l x 10^{-6}	M_1 $sec.^{-1}$	$\frac{1}{M_1}$ sec.
135	5.36	1.865	.055	18.2
136	5.36	1.865	.0547	18.3
138	5.31	1.885	.0658	15.2
139	5.31	1.885	.0569	17.6
121	10.34	0.970	.0864	11.6
122	10.34	0.970	.0864	11.6
126	11.01	0.910	.0894	11.2
127	11.01	0.910	.0886	11.3
123	11.28	0.887	.0852	11.7
124	11.25	0.890	.0888	11.25
141	12.0	0.837	.0906	11.05
142	11.9	0.842	.0981	10.2
144	15.34	0.653	.0996	10.05
145	15.26	0.656	.1066	9.43
153	30.43	0.329	.135	7.42

In Section 2.8, the temperature dependence of a second order rate constant, presumed to be the low pressure decomposition rate of benzyl iodide, was shown to have an activation energy of 40 K cal./mol. It is remarkable that such an entirely reasonable value was obtained when, in fact, the reaction was being complicated by the concurrence of the reaction I + BzI $\longrightarrow$ Bz + I_2. Using the data on the temperature dependence of this latter reaction, the previous results, (Table 19) can be recalculated on the basis of the initial dissociation reaction only.

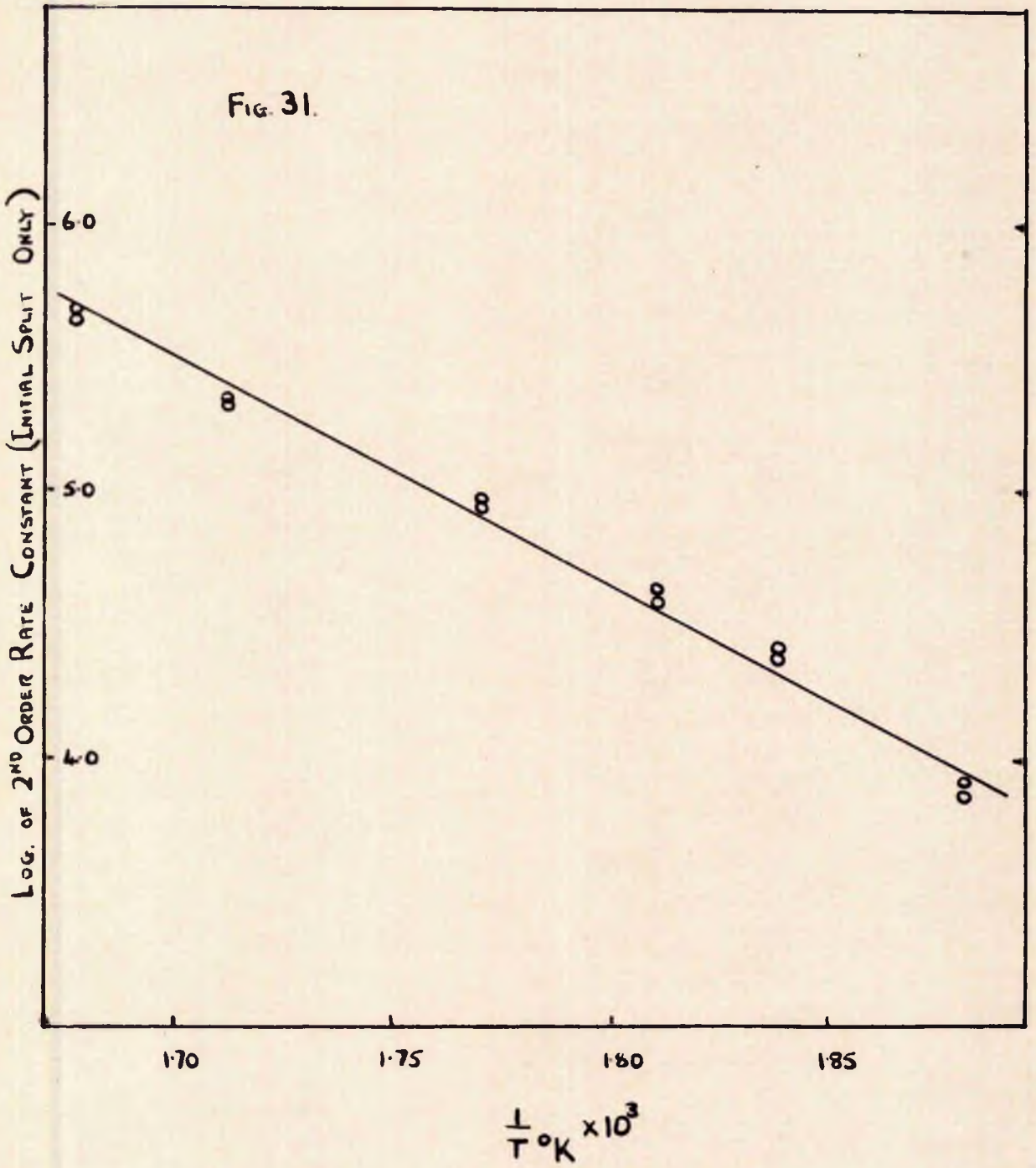


Fig. 31. Log. of 2nd Order Rate Constant (Initial Split Only) v. $\frac{1}{T°K}$

The percentages of decomposition due to this initial split have been determined and are given in Table 25 which also shows the corresponding second order rate constants. Figure 31 shows a graph of the logarithm of these second order rate constants against the reciprocal of the absolute temperature.

Table 25

HI Partial Pressures 0.12-0.25 mm.

Exp. No.	Temp. °K	(BzI) x 10^7 mols. l^{-1}	Reaction time sec.	% Decomp. due to initial dissoc.	Assumed 2nd. order rate constant x 10^{-5}	log of 2nd order rate constant
138	585	5.55	.57	6.55	2.22	5.345
139	585	5.55	.57	6.20	2.11	5.324
165	596	4.52	.58	10.75	4.56	5.66
166	596	4.52	.58	11.0	4.67	5.67
168	565	4.73	.61	2.54	0.902	4.953
169	565	4.73	.61	2.73	0.960	4.980
171	554	5.80	.71	1.56	0.385	4.573
172	554	5.80	.71	1.64	0.402	4.605
174	544	5.55	.89	1.16	0.238	4.376
175	544	5.55	.89	1.24	0.251	4.400
177	534	5.35	.95	0.38	0.0784	3.893
178	534	5.35	.95	0.37	0.0760	3.880

The data, plotted in Figure 31, form a reasonable straight line and this might be regarded as evidence that the reaction is genuinely second order in this region of low partial pressures of reactant. The activation energy, calculated from Figure 31, is 40 K cal./mol. which is in good agreement with the values obtained in Section 1 (decomposition of benzyl iodide in the absence of a radical acceptor) and in section 3.3

(from the energy of activation of the reaction $I + BzI \longrightarrow I_2 + Bz$). For this assumed second order reaction, the pre-exponential factor, in the rate expression, is $10^{20.4}$ l mol.$^{-1}$ sec.$^{-1}$. As has been noted previously (section 2.8), this apparently high value is quite consistent with this type of reaction. Slater[82] has calculated that, for the relatively simple molecule, nitryl chloride, the second order pre-exponential factor should be 1.45×10^{20} l mol.$^{-1}$ sec.$^{-1}$ and this has been substantially confirmed experimentally by Cordes and Johnston[94], who obtained the value 5.8×10^{19} l mol.$^{-1}$ sec.$^{-1}$. It might, therefore, be expected that the unimolecular decomposition of benzyl iodide would involve a second order pre-exponential factor as least as large as that for nitryl chloride.

Unfortunately, there are insufficient data on the variation of the decomposition rate with concentration of reactant, at these very low partial pressures, to prove that the reaction is accurately second order. Theoretical calculations, by Slater[82], suggest that it is, in fact, unlikely that this reaction is genuinely second order at partial pressures of ~ 0.02 mm. The good agreement of the derived activation energy with the values obtained in previous sections must, therefore, be regarded as probably being fortuitous.

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

The results of the work, described in this thesis, may be summarised as follows:-

1) The gas phase pyrolysis of benzyl iodide, either alone or in the presence of added free iodine, proceeds via the following mechanism -

(a) $BzI \overset{Ke}{\longleftrightarrow} Bz + I$

(b) $I + I \longleftrightarrow I_2$

(c) $Bz + Bz \xrightarrow{k_2} Bz\text{-}Bz$

An analysis of the data has been carried out where reactions (a) and (b) are presumed to reach equilibrium and reaction (c) is rate determining. Over a temperature range of 516°K, carried out using both static (516-557°K) and flow (611-702°K) systems with benzyl iodide partial pressures from .03 mm. to 9.0 mm., the logarithm of $2 k_2 K_e^2$ plotted against $\frac{1}{T°K}$ gave a straight line. The slope of this line on the above mechanism is equal to $\frac{2\Delta H + E}{2.3 R}$ (where ΔH = change in heat content associated with the equilibrium $BzI \longleftrightarrow Bz + I$ and E = the activation energy of the reaction $Bz + Bz \longrightarrow Bz\text{-}Bz$) and $(2\Delta H + E)$ was found to be 84 K cal./mol. On the assumption that E = 0, this is equivalent to a benzyl iodide bond strength of 42 K cal./mol. This experimentally derived bond strength must be reduced by 1 K cal./mol. for every 2 K cal./mol. of energy of activation required by the recombination of two benzyl radicals. A review of the literature, on free radical recombination energies, suggests that for benzyl radicals

it is not likely to exceed 4-5 K cal./mol. and therefore the present investigation leads to a value of 40-42 K cal./mol. for the strength of the carbon-iodine bond in benzyl iodide.

2) It has been shown that, in the presence of excess hydrogen iodide as a radical acceptor, benzyl iodide decomposes according to the following mechanism -

(a) $BzI \longrightarrow Bz + I$

(b) $I + I \longleftrightarrow I_2$

(d) $Bz + HI \longrightarrow Bz\text{-}H + I$

(e) $I + BzI \longrightarrow Bz + I_2$

In this scheme, the rate determining process is the dissociation process in (a) since, with sufficient HI present, reaction (d) prevents an equilibrium concentration of benzyl radicals being built up.

It has been shown to be possible to obtain conditions where the rate of iodine formation is independent of HI concentrations. Using such conditions, reaction (e) was shown to be a very significant contributor to the total rate. Moreover, the elimination of the back reaction in (a) produced a large increase in decomposition rate, so much so that the range of temperature used in this section of the work was over 100°C below that for the previous section.

The energy of activation of the reaction (e) has been determined as 4.1 K cal./mol. (This value was calculated from results covering the temperature range 505 to 585°K). Using Perlman and Rollefson's[78] data on the dissociation of molecular iodine, this activation energy of

4.1 K cal./mol. is equivalent to a benzyl iodide bond strength of 40.6 K cal./mol. This value is in good agreement with that obtained from the pyrolysis work in the absence of a radical acceptor.

The initial dissociation reaction (BzI $\longrightarrow$ Bz + I) has been found to be between first and second order at the partial pressures of benzyl iodide used (0.02 mm. - 0.13 mm.) and this is attributed to the normal Hinshelwood-Lindemann effect for unimolecular reactions. An approximate value of 0.35 $sec.^{-1}$ for the high pressure limiting rate constant at 585°K has been deduced. This corresponds to an Arrhenius factor for the decomposition of $10^{14.6}$ $sec.^{-1}$, if the benzyl iodide bond strength is assumed to be 40.6 K cal./mol.

3) At the very lowest partial pressures used ($\sim$0.02 mm.), the initial dissociation reaction approaches second order behaviour and the temperature dependence of assumed second order rate constants leads to an activation energy of 40 K cal./mol. for the decomposition. The corresponding pre-exponential factor is $10^{20.4}$, which is of the order of magnitude to be expected for a reaction of this type. The data, in this low pressure region, are, however, insufficient to establish that the reaction is accurately second order at these pressures.

4) If the bond strength of benzyl iodide is taken as 41 K cal./mol., as determined in this present investigation, a value may be calculated for the heat of formation of the benzyl radical. Using 27.2 K cal./mol. for the heat of formation of benzyl iodide, as suggested by Skinner[63], a value of 43 K cal./mol. is obtained for ΔH_f (Benzyl). This is in close agreement with the values of 45.3 K cal./mol. and 44.8 cal./mol.,

obtained in this Department by Alexander[58] and Davidson[59] respectively - their values were derived from their determinations of the bond strength of the central carbon-carbon bond in dibenzyl. The present value of 43 K cal./mol. is also in accord with the 44.9 K cal./mol., deduced from Benson and Buss[47] determination of the toluene bond strength as 84 K cal./mol. The more commonly quoted toluene bond strength of 77.5 K cal./mol., obtained by Szwarc[48] leads to a ΔH_f (Benzyl) of only 37.4 K cal./mol. and would, therefore, seem to be too low.

APPENDICES

APPENDIX 1

COLLECTED EXPERIMENTAL PRIMARY DATA

TABLE I

SILICA VESSEL - BENZYL IODIDE AND IODINE ONLY

Exp. No.	Temp. °K	Reaction Time secs.	pp BzI mm.	pp I_2 mm. x 10^{-2}	pp N_2 mm.	% Decomp.
3	650	.41	.074	-	4.3	5.35
4	650	.41	.074	-	4.3	5.58
7	651	.54	.068	-	4.3	6.45
8	651	.54	.068	-	4.3	6.82
9	651	.95	.090	-	4.1	8.56
10	651	.95	.090	-	4.1	8.41
13	650	.42	.077	-	4.1	5.70
14	650	.42	.077	.21	4.1	2.73
15	650	.42	.077	.21	4.1	2.90
17	650	.36	.075	-	4.3	5.36
18	650	.36	.075	.11	4.3	3.60
19	652	.31	.063	-	4.5	5.20
20	652	.31	.063	.27	4.5	2.40
21	652	.31	.063	.27	4.5	2.22
22	650	.38	.070	-	4.3	5.15
23	650	.38	.070	.23	4.3	2.42
25	650	.56	.071	-	4.3	6.02
28	650	.62	.081	-	4.1	7.53
39	651	.66	.071	-	4.3	6.90
40	651	.66	.071	-	4.3	6.97
41	651	1.20	.081	-	4.0	8.20
42	651	1.20	.081	-	4.0	8.90
44	650	.58	.076	.167	4.3	3.50
45	650	.58	.076	.167	4.3	4.00
46	651	.67	.067	-	4.1	6.85
47	651	.67	.067	.199	4.1	2.83
48	651	.67	.067	.199	4.1	3.20
49	650	.83	.070	-	4.1	7.75
50	650	.83	.070	.244	4.1	4.1
51	650	.83	.070	.244	4.1	3.97
52	674	.34	.071	-	4.3	7.50
53	674	.34	.071	-	4.3	7.12
54	674	.34	.071	.154	4.3	3.52

Exp. No.	Temp. °K	Reaction Time secs.	pp BzI mm.	pp I_2 mm. x 10^{-2}	pp N_2 mm.	% Decomp.
55	674	.37	.069	-	4.4	7.45
57	674	.37	.069	.206	4.4	2.10
61	674	.70	.094	-	4.2	12.0
62	674	.70	.094	-	4.2	12.2
64	674	.44	.065	-	4.2	8.10
65	674	.44	.065	-	4.2	8.50
67	674	.63	.080	-	4.2	10.4
68	674	.63	.080	-	4.2	10.8
69	674	.63	.080	.238	4.2	6.60
70	674	.74	.093	-	4.1	10.7
72	674	.74	.093	.425	4.1	5.89
73	673	.49	.078	-	4.4	9.32
74	673	.49	.078	-	4.4	9.42
75	673	.49	.078	.260	4.4	4.60
76	673	.86	.091	-	4.1	12.7
77	673	.86	.091	-	4.1	12.75
78	673	.86	.091	.175	4.1	7.35
79	702	.30	.072	-	4.5	18.8
80	702	.30	.072	-	4.5	19.3
81	685	.37	.075	-	4.4	11.3
82	685	.37	.075	-	4.4	9.56
83	611	.86	.085	-	4.1	1.52
84	611	.86	.085	-	4.1	1.48
85	632	.86	.086	-	4.1	4.09
86	632	.86	.086	-	4.1	4.01
87	662	.53	.096	-	4.1	8.36
88	662	.53	.096	-	4.1	8.58
89	662	.53	.096	.170	4.1	5.96
90	663	.60	.112	-	4.2	8.30
91	663	.60	.112	-	4.2	8.10
92	663	.60	.112	.200	4.2	5.05
93	663	.36	.041	-	4.4	5.80
94	663	.36	.041	-	4.4	5.73
95	663	.36	.041	.141	4.4	3.84
96	663	.83	.032	-	4.1	8.78
97	663	.83	.032	-	4.1	8.78
98	663	.83	.032	.586	4.1	1.44
99	663	.55	.030	-	4.3	7.92
100	663	.55	.030	-	4.3	7.90
101	663	.79	.034	-	4.3	8.56
102	663	.79	.034	-	4.3	9.36
103	663	.79	.034	.104	4.3	6.38
104	662	.81	.200	-	4.1	9.70
105	662	.81	.200	-	4.1	9.70

Exp. No.	Temp. °K	Reaction Time secs.	pp BzI mm.	pp I_2 mm. x 10^{-2}	pp N_2 mm.	% Decomp.
107	663	.51	.148	-	4.3	8.30
108	663	.51	.148	-	4.3	8.57
109	663	.51	.148	.108	4.3	7.46
110	663	.37	.046	-	4.5	7.02
111	663	.37	.046	-	4.5	6.53
112	663	.37	.046	.061	4.5	4.37

TABLE II

SILICA VESSEL - BENZYL IODIDE AND HYDROGEN IODIDE

Exp. No.	Temp. °K	Reaction Time secs.	pp BzI mm.	pp HI mm.	pp N_2 mm.	% Decomp.
121	585	.54	.044	.488	3.7	12.2
122	585	.54	.044	.488	3.7	12.1
123	585	.54	.048	.388	3.7	11.9
124	585	.54	.048	.388	3.7	12.6
126	585	.58	.047	.199	3.8	13.5
127	585	.58	.047	.199	3.8	13.3
129	585	.58	.055	.084	3.8	8.7
130	585	.58	.055	.084	3.8	9.0
132	585	.55	.058	.035	3.9	4.6
133	585	.55	.058	.035	3.9	4.7
135	585	.54	.020	.266	3.5	7.6
136	585	.54	.020	.266	3.5	7.5
138	585	.57	.020	.254	3.8	9.0
139	585	.57	.020	.254	3.8	8.7
141	585	.52	.050	.455	3.7	12.6
142	585	.52	.050	.455	3.7	13.9
144	585	.51	.065	.585	3.5	14.3
145	585	.51	.065	.585	3.5	15.2
148	585	.50	.053	2.20	3.9	16.2
153	585	.50	.134	.885	3.0	20.8
156	574	.41	.047	.472	3.5	6.3
157	574	.41	.047	.472	3.5	6.7
159	574	.41	.050	.471	6.9	8.0
160	574	.41	.050	.471	6.9	8.5
162	574	.44	.050	.452	9.9	9.3
163	574	.44	.050	.452	9.9	9.4
164	574	.44	.048	.460	2.0	6.4
165	596	.58	.017	.135	3.8	15.7
166	596	.58	.017	.135	3.8	16.1
168	565	.61	.017	.121	3.8	3.4
169	565	.61	.017	.121	3.8	3.6
171	554	.71	.020	.184	3.8	2.1
172	554	.71	.020	.184	3.8	2.2
174	544	.89	.019	.156	3.7	1.5
175	544	.89	.019	.156	3.7	1.6
177	534	.95	.019	.185	3.6	0.58
178	534	.95	.019	.185	3.6	0.56
183	554	.71	.069	.770	6.3	5.4
184	554	.71	.069	.770	6.3	5.7

Exp. No.	Temp. °K	Reaction Time secs.	pp BzI mm.	pp HI mm.	pp N_2 mm.	% Decomp.
186	555	.71	.030	.815	6.3	3.3
187	555	.71	.030	.815	6.3	3.5
189	554	.75	.019	.847	6.2	2.2
190	554	.75	.019	.847	6.2	2.0
192	555	.68	.020	.788	9.5	2.4
193	555	.68	.020	.788	9.5	2.4
195	554	.71	.062	.790	9.4	6.1
196	554	.71	.062	.790	9.4	6.3
198	554	.70	.037	.794	9.6	4.4
200	554	.70	.037	.794	9.6	4.4
201	554	.69	.087	.810	9.4	8.5
202	554	.66	.087	.810	9.4	8.4
204	554	.75	.113	.860	9.2	10.2
205	554	.75	.113	.860	9.2	10.5
207	554	.73	.053	.850	9.5	5.9
208	554	.73	.053	.850	9.5	6.0

TABLE III

SILICA VESSEL - BENZYL IODIDE, HYDROGEN IODIDE PLUS INERT GASES

Exp. No.	Temp. °K	Reaction Time secs.	pp BzI mm.	pp HI mm.	pp N_2 mm.	pp PhH mm.	pp CH_3I mm.	% Decomp.
223	559	.44	.011	.482	1.54	1.88	-	1.52
225	559	.44	.011	.482	1.54	1.88	-	1.59
227	558	.42	.013	.471	1.55	0.75	-	1.05
228	558	.42	.013	.471	1.55	0.75	-	1.13
229	559	.42	.013	.462	1.47	2.52	-	1.97
230	559	.42	.013	.462	1.47	2.52	-	2.02
232	559	.45	.015	.510	1.52	1.13	-	1.54
233	559	.45	.015	.510	1.52	1.13	-	1.67
238	558	.42	.012	.452	1.57	-	1.40	0.94
239	558	.42	.012	.452	1.57	-	1.40	0.97
241	558	.44	.012	.450	1.58	-	0.99	1.04
243	558	.44	.012	.450	1.58	-	0.99	0.95
246	558	.40	.012	.450	1.53		2.20	1.22
247	558	.40	.012	.450	1.53		2.20	1.03

TABLE IV

PYREX VESSEL - BENZYL IODIDE AND HYDROGEN IODIDE

Exp. No.	Temp. °K	Reaction Time secs.	pp BzI mm.	pp HI mm.	pp N_2 mm.	% Decomp.	No. of liners
249	565	.77	.016	.627	3.3	5.95	0
250	565	.77	.016	.627	3.3	6.16	0
256	565	.69	.016	.544	3.3	8.15	1
257	565	.69	.016	.544	3.3	8.27	1
258	565	.71	.016	.561	3.2	9.95	2
259	565	.71	.016	.561	3.2	10.0	2
260	574	.71	.016	.561	3.2	15.8	2
261	535	.76	.017	.566	3.1	6.20	2
262	535	.76	.017	.566	3.1	5.74	2
263	522	.78	.017	.566	3.1	3.55	2
264	517	.79	.016	.535	3.2	3.57	2
265	517	.79	.016	.535	3.2	3.74	2
266	535	.77	.016	.535	3.2	6.11	2
267	575	.70	.017	.561	3.3	19.1	2
268	575	.70	.017	.561	3.3	18.4	2
272	489	.89	.017	.621	3.1	2.23	2
273	489	.89	.017	.621	3.1	2.16	2
274	533	.83	.017	.595	3.2	2.94	0
275	533	.83	.017	.595	3.2	2.90	0
276	579	.77	.015	.586	3.2	10.6	0
277	579	.77	.015	.586	3.2	10.6	0
278	587	.76	.015	.586	3.2	14.7	0
279	505	.88	.015	.566	3.3	1.03	0
280	505	.88	.015	.566	3.3	1.13	0
*282	536	.81	.016	.576	3.3	3.46	0

* Reaction Vessel coated with Carbon

TABLE V

SILICA VESSEL - BENZYL IODIDE, HYDROGEN IODIDE AND IODINE

Exp. No.	Temp. °K	Reaction Time secs.	pp BzI mm.	pp HI mm.	pp I_2 mm x 10^{-2}	pp N_2 mm.	% Decomp.
292	574	.51	.017	.570	-	3.3	5.85
293	574	.51	.017	.570	.216	3.3	8.35
294	574	.51	.017	.570	.216	3.3	8.15
296	574	.51	.016	.600	.292	3.3	7.78
297	574	.51	.016	.600	.292	3.3	8.14
298	574	.49	.015	.610	-	3.3	5.09
299	574	.49	.015	.610	.556	3.3	7.67
300	574	.49	.015	.610	.556	3.3	7.90
302	585	.49	.015	.580	-	3.3	7.85
303	585	.49	.015	.580	.265	3.3	13.2
304	585	.49	.015	.596	-	3.3	7.80
305	585	.49	.015	.596	.575	3.3	14.1
306	585	.49	.015	.596	.575	3.3	13.1
307	536	.52	.016	.566	-	3.4	0.75
308	536	.52	.016	.566	.192	3.4	1.60
309	536	.52	.016	.566	.192	3.4	1.23
310	536	.54	.017	.500	-	3.4	1.00
311	536	.54	.017	.500	.099	3.4	1.65
312	536	.54	.017	.500	.099	3.4	1.73
313	536	.52	.016	.570	-	3.3	0.95
314	536	.52	.016	.570	.091	3.3	1.30
315	505	.53	.015	.555	.186	3.3	0.64
316	505	.53	.015	.555	.186	3.3	0.68

APPENDIX 2

THEORY OF UNIMOLECULAR REACTIONS

Hinshelwood-Lindemann Mechanism for Unimolecular Reactions

It is postulated that the activation of the reactant A takes place as follows:-

$$A + A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A^* + A$$

$$A^* \xrightarrow{k_3} \text{Products}$$

where A^* is an activated molecule with sufficient energy to decompose.

Under stationary state conditions,

$$(A^*) = \frac{k_1 (A)^2}{k_2 (A) + k_3}$$

and then $$- \frac{d(A)}{dt} = k_3 (A^*) = \frac{k_1 k_3 (A)^2}{k_2 (A) + k_3}$$

Two extreme conditions may be considered

i) $k_2 (A) \gg k_3$. This is equivalent to assuming that A^* de-activates much more readily than it decomposes and thus

$$- \frac{d(A)}{dt} = \frac{k_1 k_3 (A)}{k_2}$$

i.e. a first order decomposition at high pressures of A.

ii) $k_3 \gg k_2 (A)$. Reaction and not de-activation is the prominent step in this case.

$$\text{Thus} \quad -\frac{d(A)}{dt} = \frac{k_1 k_3}{k_3} (A)^2 = k_1 (A)^2$$

i.e. a second order reaction which occurs at low pressures of A.

Effect of Inert Gases on Unimolecular Reactions

The simple Hinshelwood-Lindemann, outlined above, does not predict any affect of inert gases. However, it is readily extended to include the core of activation by an inert gas molecule and the theory given here is a simplified version of that used by Johnston.

Let A be the reacting molecule and X, Y, ... inert gas molecules. Then the following reaction may take place:-

$$A + A \xrightarrow{k_1} A^* + A$$
$$A + X \xrightarrow{k_{1X}} A^* + X$$
$$A + Y \xrightarrow{k_{1Y}} A^* + Y$$
$$A^* + A \xrightarrow{k_2} A + A$$
$$A^* + X \xrightarrow{k_{2X}} A + X$$
$$A^* + Y \xrightarrow{k_{2Y}} A + Y$$
$$A^* \xrightarrow{k_3} \text{Products}$$

Setting up a stationary state as before

$$(A^*) = \frac{k_1 (A)^2 + k_{1X} (A)(X) + k_{1Y} (A)(Y) + \cdots\cdots}{k_3 + k_2 (A) + k_{2X} (X) + k_{2Y} (Y) + \cdots\cdots}$$

and hence $$- \frac{d (A)}{dt} = k_3 (A^*) = \frac{k_3 \left[k_1 (A)^2 + k_{1X} (A)(X) + k_{1Y} (A)(Y) + \cdots\cdots\right]}{k_3 + k_2 (A) + k_{2X} (X) + k_{2Y} (Y) \cdots\cdots}$$

and if we assume a unimolecular rate constant k for the decomposition of A, we have

$$- \frac{d (A)}{dt} = k (A)$$

Under conditions where the rate of decomposition of (A^*) is much greater than its rate of de-activation,

$$k_3 \gg k_2 (A) + k_{2X} (X) + k_{2Y} (Y) + \cdots\cdots$$

and then,

$$- \frac{d (A)}{dt} = k (A) = k_1 (A)^2 + k_{1X} (A)(X) + k_{1Y} (A)(Y) \cdots\cdots$$

$$\therefore \quad k = k_1 (A) + k_{1X} (X) + k_{1Y} (Y) + \cdots\cdots$$

For a system consisting of the reacting gas A and one inert gas X, we have

$$k = k_1 (A) + k_{1X} (X)$$

If the concentration of A is maintained constant and the concentration of X is varied while still obeying the condition that

$$k_3 \gg k_2 (A) + k_{2X} (X)$$

then, a graph of the assumed first order rate constant k, against the

concentration of X, should be a straight line. The slope of this line is k_{1X} and the intercept, on the (X) = 0 axis, is k_1 (A). The efficiency, α_X, of the inert gas, X, in transferring energy to A relative to the efficiency of A itself is given by

$$\alpha_X = \frac{k_{1X}}{k_1}$$

Thus, from the graph of k versus (X)

$$\alpha_X = \frac{\text{(slope of line) (concentration of A)}}{\text{Intercept on (X) = 0 axis}}$$

It has already been shown that

$$k\,(A) = \frac{k_3\left[k_1\,(A)^2 + k_{1X}\,(A)(X) + k_{1Y}\,(A)(Y) + \cdots\right]}{k_3 + k_2\,(A) + k_{2X}\,(X) + k_{2Y}\,(Y) + \cdots}$$

$$\frac{1}{k} = \frac{1}{k_1\,(A) + k_{1X}\,(X) + k_{1Y}\,(Y) \cdots} + \frac{k_2\,(A) + k_{2X}\,(X) + k_{2Y}\,(Y) + \cdots}{k_3\left[k_1\,(A) + k_{1X}\,(X) + k_{1Y}\,(Y) + \cdots\right]}$$

Now $k_1\,(A) + k_{1X}\,(X) + k_{1Y}\,(Y) + \cdots$

$= k_1\left[(A) + {}_X(X) + {}_Y(Y) + \cdots\right]$

$= k_1\left[\text{effective pressure}\right]$

Thus a plot of $\frac{1}{k}$ versus $\frac{1}{\text{effective pressure}}$ should be a straight line whose slope is $\frac{1}{k_1}$.

APPENDIX 3

EFFECT OF SURFACE TO VOLUME RATIO OF REACTOR ON THE DECOMPOSITION OF BENZYL IODIDE IN THE PRESENCE OF HYDROGEN IODIDE

Szwarc[1] showed that, in the simple pyrolysis of benzyl iodide, there was no wall effect, even when the surface to volume ratio of his Pyrex reaction vessel was increased twelvefold by the use of Pyrex wool. This is confirmed with respect to the nature of the wall by the fact that the results of the present investigation, in a silica vessel, agree closely with those of Szwarc.

The above experiments were confined to investigations of the decomposition of benzyl iodide alone and do not necessarily apply in the presence of HI, as a radical acceptor. When HI is present, there is the possibility that first to second order transitions will occur in the primary decompositin reaction at low partial pressures of reactant - these transitions can, of course, only be observed when the radical acceptor prevents the occurrence of the reverse reaction. Other workers at St. Andrews, have shown that, in similar cases, a wall effect is observed. For example, Lapage[5] found an increase in the decomposition rate of methyl iodide with increasing surface area to volume ratio but she observed no change in the energy of activation of the decomposition. This work was later confirmed by Cundall[6] and very similar results were obtained by Downs[7] for the decomposition of trifluoromethyl iodide. In all these cases, the increase in reaction observed was attributed to the activating effect of the surface on a reaction which was in the transition region between first and second

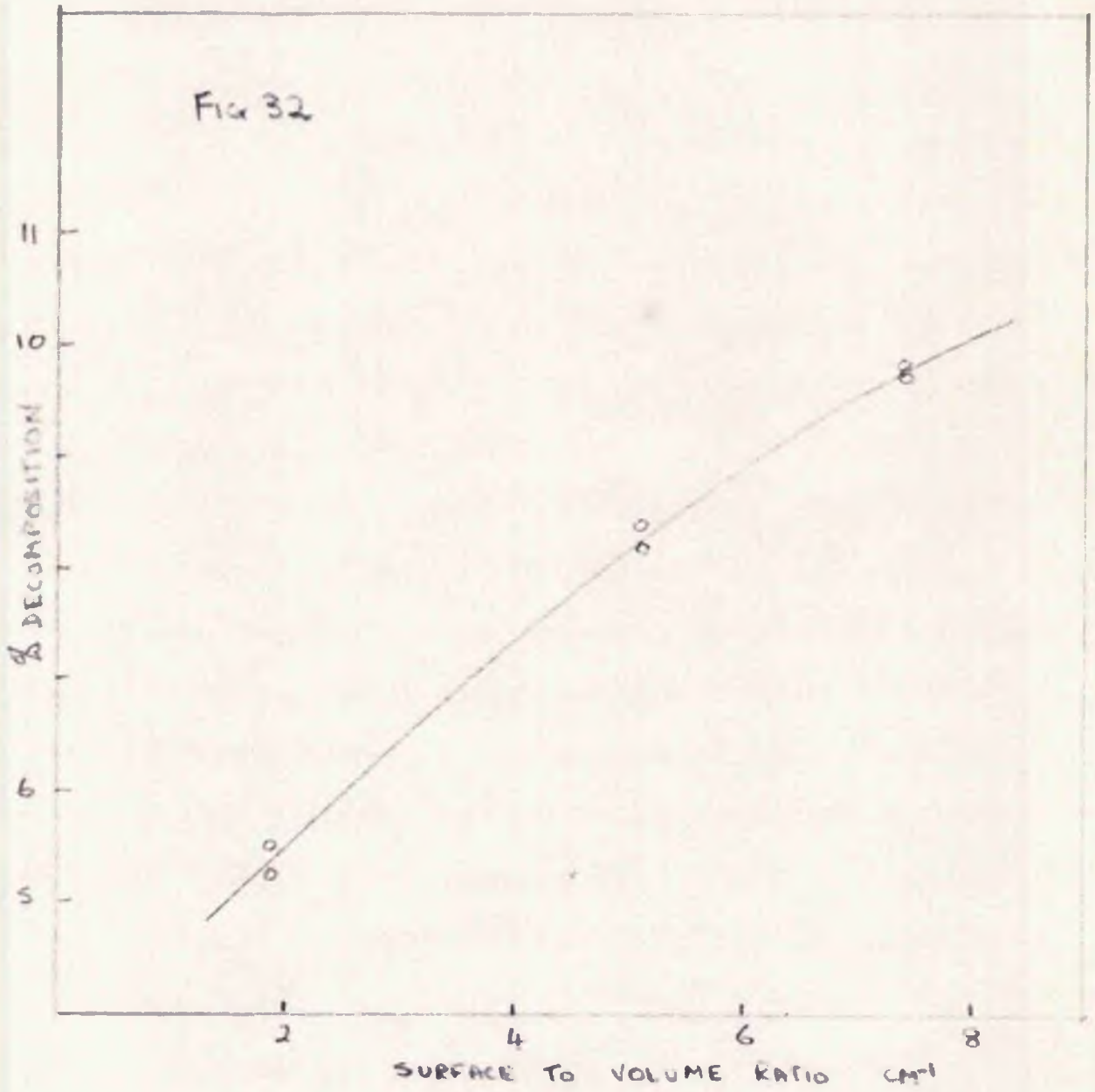


Fig 32 Effect of surface area on % decomposition.

order. All this evidence suggested that a test should be made to determine whether BzI, when in the presence of excess HI (and thus devoid of any complicating reverse reaction), showed similar effects.

Because it is easier to construct internal sleeves for a reaction vessel in Pyrex, the silica vessel, which was used in all the other experiments, was replaced with a Pyrex one with detachable ends. Initially, three experiments were carried out under identical conditions, except that the surface area to volume ratio was varied by the insertion of either one or two sleeves into the reaction vessel, and the results are shown in Figure 32 . (The experimental conditions were:- BzI partial pressure, .0155-.0157 mm., HI pressure 0.54-0.63 mm., N_2 pressure 3.2-3.3 mm., temperature 565°K and reaction time 0.69-0.77 sec. Detailed results of each of these experiments and all the others in this Appendix are included in the comprehensive results tables in Appendix 1). It is evident, from Figure 32, that a pronounced increase in the rate of reaction occurs with increasing surface area. This effect is similar to that observed for methyl and trifluoromethyl iodides.

In order to investigate this wall effect in more detail, experiments were carried out over a range of temperatures, both in the Pyrex vessel itself and the same vessel with two Pyrex liners inserted. In these experiments, low partial pressures of benzyl iodide (~ 0.02 mm.) were used in order to compare the results directly with those obtained in the previous work (see pages 93 - 95) in which a silica vessel was used. The results are shown in Figure 33 in which the logarithm of an assumed second order reaction (as it was then thought to be) constant is plotted against the reciprocal of the absolute temperature. The

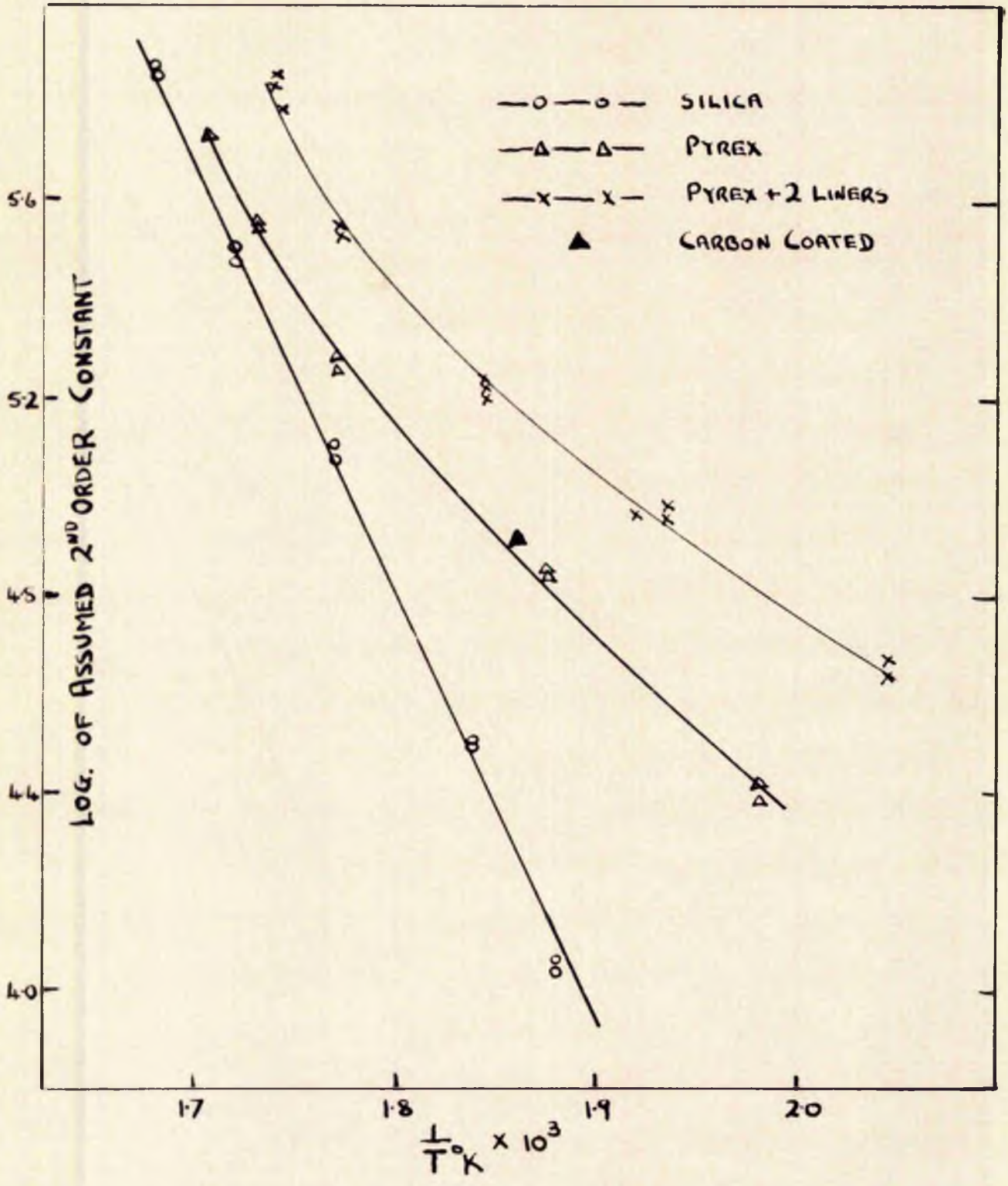


FIG. 33. EFFECT OF SURFACE ON REACTION RATE

previous data, for the silica vessel, are included on the graph for comparison. It is obvious, from Figure 33, that not only is the absolute rate of this reaction surface dependent but the activation energy is apparently less in Pyrex than it was in silica.

In respect of the apparent change in activation energy, these results differ markedly from the results with methyl and trifluoromethyl iodides where no change in activation energy was noted, although the decompositions were surface dependent. It seems unlikely, therefore, that the explanation of this 'wall effect' can be simply that it is an activating effect of the surface on a first to second order transition. The only other explanation, which seems likely, is that the wall is exerting a catalytic effect, either on the initial decomposition reaction or on the subsequent iodine atom-benzyl iodide molecule interaction. Such an explanation could account for the lower activation energy observed in Pyrex. It will be noted, from Figure 33, that the curves for the Pyrex vessel approach that for the silica vessel at high temperatures and this may indicate that there are two reactions, one of which is homogeneous and the other heterogeneous. If the heterogeneous reaction had a lower energy of activation but a smaller A factor than the homogeneous one, then the former would become less important as the temperature increased and this could explain the convergence of the Pyrex and silica data at high temperatures.

An isolated experiment, in which the Pyrex vessel was coated with carbon, failed to show any significant change in the rage of decomposition. In spite of this result, it is considered that an

explanation in terms of a catalytic effect of the surface is the most likely.

It should be stressed that no such 'wall effect' was evident in the experiments in which no HI was added and this can, presumably, be attributed to the fact that an equilibrium is attained in the system $BzI \longleftrightarrow Bz + I$.

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